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HAFNIUM

[7440-58-6]

Symbol: Hf; atomic number 72; atomic weight 178.49; a Group IV B (Group 4) transition metal element; atomic radius 1.442Å; electron configuration [Xe]4f¹⁴5d²6s²; common valence +4, also exhibits oxidation states +2 and +3; most abundant natural isotope Hf-180; isotopes and their natural abundances: Hf-176 (5.21%), Hf-177 (18.56%), Hf-178 (27.10%), Hf-179 (13.75%), Hf-180 (35.22%), artificial isotopes 157, 158, 168, 173, 175, 181–183.

History, Occurrence, and Uses

Hafnium was discovered in 1922 by Coster and deHevesy. They named it for Hafnia, the Latin word for Copenhagen. It is found in all zirconium ores, such as zircon, (ZrSiO₄) and baddeleyite (ZrO₂). It occurs in the earth's crust at about 3 mg/kg. Its average concentration in sea water is 7 ng/L.

Hafnium is used in control rods for nuclear reactors. It has high resistance to radiation and also very high corrosion resistance. Another major application is in alloys with other refractory metals, such as, tungsten, niobium and tantalum.

Physical Properties

Occurs as a close-packed hexagonal alpha-form and a body-centered cubic beta modification; melting point 2,233°C; vaporizes at 4,602°C; electrical resistivity 35.5 microhm-cm at 20°C; magnetic susceptibility 0.42x10⁻⁶ emu/g at 25°C; thermal neutron absorption cross section 105 barns/atom; work function 3.5 eV; modulus of elasticity 20x10⁶ psi; tensile strength 58,000 psi at 25°C; insoluble in water, dilute mineral acids and nitric acid at all concentrations; soluble in hydrofluoric acid, concentrated sulfuric acid and aqua regia.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (g)	148.0 kcal/mo
ΔG_f° (cry)	0.0
ΔG_f° (g)	137.8 kcal/mol
S° (cry)	10.41 cal/degree mol
S° (g)	44.64 cal/degree mol
C_p (cry)	6.15 cal/degree mol
C_p (g)	4.97 cal/degree mol
H_{fus}	6.5 kcal/mol
H_{vap}	72.0 kcal/mol
Coeff. linear expansion	5.9x10 ⁻⁶ /°C
Thermal conductivity (at 50°C)	0.0533 cal/sec/cm/°C

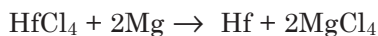
Production

Hafnium is obtained commercially from mineral zircon, which is zirconium orthosilicate [14940-68-2]. Zircon usually contains hafnium oxide, HfO₂, in an amount that ranges between 1 to 2%. Zircon sand is separated from heavy

mineral fractions from alluvial deposits by various electrostatic and magnetic separation processes. The sand is then ground and heated with caustic soda at 600°C or with soda ash at 1,000°C, or fused with lime at elevated temperatures to separate silicates. Alternatively, zircon may be decomposed by heating with chlorine in the presence of coke at 1,100°C. In the caustic fusion process, pulverized fusion cake is washed with water to remove water-soluble sodium silicate and unreacted caustic soda, leaving behind insoluble hydrous zirconium oxide. Hydrous zirconium oxide is soluble in most acids. It is dissolved in hydrochloric acid and filtered to remove unreacted ore and silica. When the chlorination process is applied, the products are zirconium tetrachloride, hafnium tetrachloride, and silicon tetrachloride. Silicon tetrachloride is more volatile than the other two chlorides and, therefore, zirconium tetrachloride and hafnium tetrachloride can be removed from silicon tetrachloride by condensing under controlled heating. The condensed tetrachlorides are dissolved in water and filtered to remove insoluble matter.

Aqueous extracts from caustic fusion or chlorination now contain zirconium and hafnium chlorides. Separation of these metals is carried out by counter-current liquid-liquid extraction using methyl isobutyl ketone (MIBK). The mixed chlorides are treated with an aqueous solution of ammonium thiocyanate. Oxychlorides of both the metals are formed which complex with thiocyanate ions. Hafnium oxychloride, HfOCl_2 is extracted into MIBK phase, leaving ZrOCl_2 in aqueous phase. Small amounts of zirconium (~2%) that are extracted with hafnium into the MIBK phase are stripped with HCl. Hafnium is converted to hafnium sulfate by treatment with H_2SO_4 and removed from the organic phase. Hafnium sulfate is treated with NH_4OH to convert it to hafnium hydroxide, $\text{Hf}(\text{OH})_4$. The hydroxide is heated in a kiln at 650°C to yield oxide, HfO_2 . The oxide is palletized with carbon and chlorinated to the tetrachloride, HfCl_4 . The HfCl_4 is sublimed and purified by passing vapors through a salt bath consisting of NaCl 10%, KCl 10%, and HfCl_4 80%, at 370°C. This removes aluminum, iron and other metal impurities.

Purified HfCl_4 is sublimed and reduced with magnesium by passing the vapors through molten magnesium heated in an electric furnace:



The product magnesium tetrachloride and any unreacted magnesium are removed from hafnium sponge produced above by distillation under vacuum. Sodium may be used instead of magnesium in the reduction reaction. Hafnium sponge may be melted in an electric furnace for further refining and the molten material may be electrolyzed to obtain ductile metal. Highly pure metal also can be obtained by reaction with iodine vapor at 600°C and the vapor of the product HfI_4 is decomposed on hafnium wire filament at 1,600°C into the metal and iodine vapor.

Reactions

The chemical properties of hafnium are very much similar to those of zirconium. In aqueous solutions, the metal exists in tetravalent state. The elec-

trode potential for the reaction $\text{Hf} \rightarrow \text{Hf}^{4+} + 4\text{e}^-$ is -1.70V . The metal in bulk form does not react with most reagents at ordinary temperatures. However, the powdered metal or hafnium sponge may readily burn in air after ignited with a spark. When heated at 360°C under water pressure, the metal is oxidized to hafnium oxide, forming a thin, protective, surface oxide layer. A similar surface hafnium oxide layer forms in nitric acid, which protects the metal from acid attack.

Reaction with hydrofluoric acid at ordinary temperatures yields hafnium tetrafluoride, HfF_4 .

In finely divided form, hafnium is pyrophoric, igniting in air spontaneously. However, bulk metal reacts slowly in oxygen or air above 400°C . The rate of oxidation increases with temperature. The product is hafnium dioxide, HfO_2 . It combines with nitrogen, carbon, boron, sulfur and silicon at very high temperatures to form hafnium nitride HfN , hafnium boride HfB , hafnium sulfide HfSi_2 , respectively. Nitride formation occurs at 900°C .

Reaction with hydrogen occurs around 700°C . Hafnium absorbs rapidly, forming a hydride which probably has a composition $\text{HfH}_{1.86}$.

Hafnium metal reacts very slowly in concentrated sulfuric acid at ordinary temperatures. At acid concentration above 70% and under boiling conditions, sulfuric acid readily attacks the metal.

Analysis

Hafnium may be measured by atomic absorption and emission spectroscopy, x-ray fluorescence, ICP-MS methods, and neutron activation. Such instrument methods are faster than wet methods and can measure the metal at trace levels.

HAFNIUM DIOXIDE

[12055-23-1]

Formula: HfO_2 ; MW 210.49

Synonym: hafnium(IV) oxide; hafnia

Uses

Hafnium dioxide is a high temperature refractory material. It is used for control rods in nuclear reactors. It has high stability and high thermal neutron absorption values. It also is used in special optical glasses and glazes.

Physical Properties

White crystalline solid, when heated at $1,500^\circ\text{C}$, it transforms into a tetragonal modification with shrinkage; tetragonal form converts to a cubic polymorph with fluorite structure when heated at $2,700^\circ\text{C}$; density 9.68 g/cm^3 ; melts at $2,774^\circ\text{C}$; insoluble in water; dissolves slowly in hydrofluoric acid at ordinary temperatures.

Preparation

Hafnium dioxide may be prepared by heating the metal with air or oxygen

at elevated temperatures (above 400°C). Also, the oxide can be obtained by igniting hafnium salts, such as hydroxide, oxalate, sulfate, nitride, carbide, boride or tetrachloride in air. Hafnium carbide converts to dioxide when heated with oxygen at 500°C. The commercial products generally contain about 95-97% hafnium dioxide mixed with small amount of zirconium oxide. The compound can be prepared at 99.9% purity.

Reactions

Hafnium dioxide reacts with chlorine in the presence of carbon at elevated temperatures to yield hafnium tetrachloride, HfCl_4 . When ammonium hydroxide solution is added to an acid solution of hafnium dioxide, the hydrous oxide, $\text{HfO}_2 \cdot x\text{H}_2\text{O}$ precipitates.

When heated with concentrated sulfuric acid, the product is hafnium sulfate, $\text{Hf}(\text{SO}_4)_2$.

Reaction with carbon at 1,500°C produces hafnium carbide, HfC .

Reaction with sodium fluorosilicate, Na_2SiF_6 at elevated temperatures yields sodium fluorohafnate, Na_2HfF_6 .

Analysis

Elemental composition: Hf 84.80%, O 15.20%. Hafnium may be analyzed in aqueous solution following digestion with hydrofluoric acid–nitric acid, or with aqua regia. The dioxide may be characterized nondestructively by x-ray methods.

HAFNIUM TETRACHLORIDE

[13499-05-3]

Formula: HfCl_4 ; MW 320.30; tetrahedral and mononuclear structure in gas phase, halide bridging polymeric structure in solid phase.

Synonym: hafnium(IV) chloride

Uses

Hafnium tetrachloride is an important intermediate in production of hafnium metal. It also is used to prepare many hafnium compounds.

Physical Properties

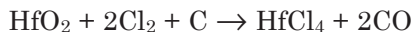
White monoclinic crystal; sublimes at 317°C; melts at 432°C at 33 atm (triple point); critical temperature 452.5°C; critical pressure 53.49 atm; critical volume 314 cm^3/mol ; hydrolyzes in water.

Thermochemical Properties

ΔH_f° (cry)	−236.7 kcal/mol
ΔH_f° (g)	−211.4 kcal/mol
ΔG_f° (cry)	−215.4 kcal/mol
S° (cry)	45.60 cal/degree mol
C_p (cry)	28.80 cal/degree mol

Preparation

Hafnium tetrachloride can be prepared (i) by chlorination of hafnium dioxide in the presence of carbon:



It also may be prepared by several other methods, such as (ii) reaction of carbon tetrachloride with hafnium dioxide above 450°C; (iii) heating a mixture of hafnium dioxide and carbon above 700°C; and (iv) reaction of chlorine with hafnium at elevated temperatures.

Reactions

Hafnium tetrachloride reacts with water at room temperature, forming hafnium oxide chloride, HfOCl_2 , and hydrochloric acid:



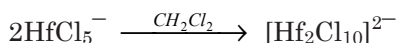
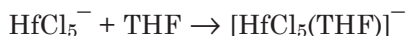
When heated with hafnium metal, the tetrachloride forms low-valence chlorides of hafnium, the dichloride and trichloride, HfCl_2 and HfCl_3 .

At elevated temperatures and in vapor phase, the tetrachloride reacts with air or steam forming finely divided hafnium dioxide, HfO_2 . When heated with boron trichloride and hydrogen to very high temperatures (above 2,000°C) hafnium diboride, HfB_2 , a gray crystalline solid, forms.

Reaction with methane at 2,100°C produces hafnium carbide, a dark-gray, brittle solid, which is not a true stoichiometric compound. It probably is a homogeneous mixture in which carbon impregnates interstitial sites in the face-centered cubic lattice of hafnium.

Hafnium tetrachloride combines with molten sodium chloride, potassium chloride, or other alkali halides to form addition products such as $2\text{NaCl} \cdot \text{HfCl}_4$, which decompose at higher temperatures.

Hafnium tetrachloride forms many octahedral complexes of structure HfCl_4L_2 with neutral donors. For example, with tetrahydrofuran, it forms $\text{HfCl}_4(\text{THF})_2$. Mononuclear and dinuclear hafnium chloride ions have been reported, produced by reaction with triphenylchloromethane, CPh_3Cl (Pampaloni, G. O. 1996. *J. Organomet. Chem.* 518, 189).

**Analysis**

Elemental composition: Hf 55.73%, Cl 44.27% The acid extract of hafnium tetrachloride may be analyzed for hafnium by AA or other instrumental methods (See Hafnium).

HAFNIUM TETRAFLUORIDE

[13709-52-9]

Formula: HfF_4 ; MW 254.48

Synonym: hafnium(IV) fluoride

Physical Properties

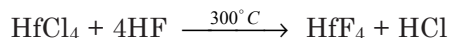
White monoclinic crystals; refractive index 1.56; density 7.1 g/cm³; sublimates at 970°C.

Thermochemical Properties

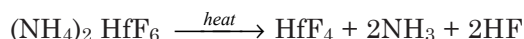
ΔH_f°	-461.4 kcal/mol
ΔG_f°	-437.5 kcal/mol
S°	27.0 cal/degree mol

Preparation

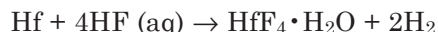
Hafnium tetrafluoride may be prepared by passing anhydrous hydrogen fluoride over hafnium tetrachloride at 300°C:



Another method of preparation involves thermal decomposition of ammonium fluorohafnate, $(\text{NH}_4)_2 \text{HfF}_6$ [16925-24-9] in the absence of air:



Also, HfF_4 can be prepared by treating metallic hafnium with 40% aqueous HF. The monohydrate formed may be heated at 350°C for several days under a flow of fluorine and nitrogen to yield anhydrous HfF_4 .

**Analysis**

Elemental composition: Hf 70.14%, F 29.86%. The compound is digested with aqua regia, the acid extract diluted and analyzed for Hf by various instrumental methods (see Hafnium). The compound may be characterized nondestructively by x-ray methods.

HELIUM

[7440-59-7]

Symbol: He; atomic number 2; atomic weight 4.0026; a Group 0 (Group 18) inert gas element; second lightest element; electron configuration 1s²; valence 0; no chemical compound known; atomic radius 0.33Å; isotope He-3 is found in trace concentration in He-4; natural abundance of He-3 1.37 ppm; short-lived radioisotopes He-5, He-6, and He-8 are known.

History, Occurrence, and Uses

Janssen and Norman Lockyer in 1868 detected helium gas in the sun's atmosphere from their spectroscopic observation. The element was named helium by Lockyer and Frankland after Helios, the Greek word for sun. Ramsey found the element in 1895 in a sample of cleveite, a uranium mineral, after removing nitrogen and oxygen by treatment with sulfuric acid. Examination of the spectrum showed a yellow line for helium along with the spectral line for argon. Swedish chemists Cleve and Langlet also discovered helium in mineral uranium.

Helium occurs in great abundance in all stars in the universe. Except for hydrogen, it is the second most abundant element in the universe. Stars derive their energy from thermonuclear conversion of hydrogen into helium. Our sun is composed of 20% helium. However, in the earth's atmosphere helium is present only in trace amounts, 5.24 ppm. Its abundance in the earth's crust is only 8g/kg. In seawater, it occurs at a concentration of 0.007 μ g/L.

The origin of helium on earth is attributed to alpha decay of uranium, thorium and other radioactive materials in the earth's crust. An alpha particle is a single charged helium ion, He^+ , which readily converts into a helium atom in its passage through the earth's crust. Helium occurs in varying concentrations in many natural gas fields. In the United States, some natural gas deposits are found to contain helium at up to 8% by volume, mostly associated with nitrogen and hydrocarbon gases.

Helium has several important industrial applications in analytical chemistry, metallurgy, space research, medicine, and low-temperature supercooling. Liquid helium is used as a cryogenic fluid for supercooling and low temperature cooling baths. Helium-3 is used as a circulating medium in laboratory refrigerators to maintain constant temperatures below 3°K. Gaseous helium is used as a carrier for gas chromatographic analysis and as a purging gas for measuring volatile organics. It is used as a lifting gas in buoyant airships and in most types of balloons, such as weather-, toy-, kite-type-, and advertising balloons. Its lifting power is just slightly less than that of hydrogen.

In metallurgy, helium is used to provide an inert atmosphere for growing crystals of high purity silicon and germanium for making transistors and diodes; as an inert shield for arc welding of metals; and to sparge dissolved gas from molten metals during purifications. In nuclear physics, helium ions or alpha particles serve as projectiles in bombarding heavy nuclei to produce energy or to obtain artificial radioisotopes. It also is used for heat transfer and coolant in nuclear reactors. Some other applications of helium include: detecting leaks in pressure containers and high-vacuum equipment; in lasers; in luminous signs for advertising; to fill space between lenses in optical instruments non-reactively; to provide an inert atmosphere for chemical reactions in the absence of air; to displace fuels and oxidizers from storage tanks in rockets or to introduce fuels into combustion chambers under helium pressure; as a non-nitrogen diluent for oxygen in SCUBA diving (so divers avoid the bends); and to mix with oxygen for treatment of respiratory diseases. Liquid helium is used in magnetic resonance imaging (MRI) equipment for diagnosis of cancer and other soft tissue diseases.

Physical Properties

Colorless and odorless gas; refractive index 1.000036 at 0°C and 1 atm; density of the gas at 0°C and 1 atm 0.1785 g/L; density of liquid helium at its boiling point 0.16 g/mL; liquefies at -268.93°C; solidifies at -272.2°C (at 26 atm) to a crystalline, transparent and almost invisible solid having a sharp melting point; cannot be solidified at the atmospheric pressure except by lowering temperatures; critical temperature -267.96°C; critical pressure 2.24 atm; critical volume 57cm³/mol; very slightly soluble in water; solubility in water 0.0285 mg/L (calculated) at 25°C or 0.174 mL/L at NTP; insoluble in ethanol.

Liquid Helium

Liquid helium exists in two forms, Helium I and Helium II. The gas liquefies at 4.22°K at 1 atm to a colorless liquid known as Helium I. The refractive index of this liquid is 1.026, which is very close to that of the gas, thus making the surface of the liquid difficult to see. Most metal wires when placed in liquid helium or at Helium I temperature exhibit superconductivity; that is, frictionless flow of electrons—flow of electrical current without any resistance whatsoever.

When the temperature of Helium I is further lowered, usually by evacuation of the system to 3.83 torr, an unusual transition occurs at 2.174°K. At this temperature, a liquid called Helium II is obtained. This liquid has many unusual properties that are different from Helium I. While Helium I is a normal fluid exhibiting the boiling of a cryogenic fluid, Helium II is a “superfluid” that has an extremely high thermal conductivity, expands on cooling and can flow rapidly through channels 10⁻⁶ cm wide. While the viscosity of helium I is about 25.5 micropoise at 2.2°C, that of Helium II is less than 10.5 micropoise. (The viscosity of water at 20°C is about 10,000 micropoise.)

Thermochemical Properties

ΔH_f°	0.0
S°	30.16 cal/degree mol
C_p	4.97 cal/degree mol

Production

Helium is produced mostly by extraction from natural gas. The process involves cooling the stream of natural gas at sufficient low temperatures and high pressures to liquefy and separate all hydrocarbons, nitrogen and other gases from gaseous helium. The ‘crude’ helium gas may be purified further by repeated liquefaction of methane, nitrogen and other impurities under pressure. Trace hydrocarbons may be removed by adsorption on activated charcoal at liquid nitrogen temperature. Water may be removed by drying over a dehydrating agent such as bauxite. Carbon dioxide may be removed by passing helium through a scrubbing solution containing monoethanolamine-ethylene glycol or similar substances. Trace hydrogen may be removed from helium by converting it into water by mixing with oxygen and passing the mix over a palladium catalyst. Final purification may be achieved by adsorbing remain-

ing trace contaminants over activated charcoal at liquid nitrogen temperature.

Alternatively, helium may be separated from natural gas by diffusion through permeable barriers, such as high silica glass or semipermeable membranes. The gas is supplied commercially in steel cylinders or tanks. The United States is the largest producer of helium in the world.

HOLMIUM

[7440-60-0]

Symbol: Ho; atomic number 67; atomic weight 164.93; a lanthanide series rare earth element; electron configuration $[\text{Xe}]4f^{11}6s^2$; valence state +3; metallic radius (coordination number 12) 1.767Å; atomic volume 18.78 cc/mol; ionic radius Ho^{3+} 0.894Å; one naturally occurring isotope, Ho-165.

History, Occurrence, and Uses

Soret and Delafontaine identified holmium in 1878 by examination of its spectrum. The following year, Cleve separated its oxide from Marignac's erbia, a mixture of erbium, holmium and thulium oxides. He named this element Holmium, after his native town Holmia (Stockholm). The metal was produced in 1934 by Klemm and Bommer.

Holium occurs in rare-earth minerals, such as monazite, gadolinite, xenotime, euxenite, fergusonite, and bastnasite. Its concentration in monazite is about 0.05%. Its abundance in the earth's crust is 1.3mg/kg.

Currently, holmium metal does not have much commercial application. However, because of its unusual magnetic properties, it is being used in research studies to explore the magnetic and alloying behavior of metals.

Physical Properties

Soft, lustrous metal; silver-like appearance; close-packed hexagonal crystal system; density 8.78 g/cm³; paramagnetic; magnetic moment 11.2 Bohr magnetons; melts at 1,472°C; vaporizes at 2,694°C; electrical resistivity 195 microhm-cm at 25°C; Young's modulus 6.71×10^{11} dynes/cm²; Poisson's ratio 0.255; thermal neutron cross section 64 barns; insoluble in water; soluble in acids (with reactions).

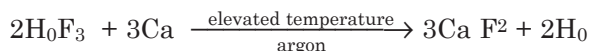
Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (g)	71.89 kcal/mol
ΔG_f° (g)	63.29 kcal/mol
S° (cry)	18.0 cal/degree mol
S° (g)	46.75 cal/degree mol
C_p (cry)	6.50 cal/degree mol
C_p (g)	4.97 cal/degree mol
ΔH_{fus}	2.81 kcal/mol
Thermal conductivity	0.106 cal/sec/cm/°C
Coeff. linear expansion (at 400°C)	$9.5 \times 10^{-6}/^\circ\text{C}$

Production

Holmium is obtained from monazite, bastnasite and other rare-earth minerals as a by-product during recovery of dysprosium, thulium and other rare-earth metals. The recovery steps in production of all lanthanide elements are very similar. These involve breaking up ores by treatment with hot concentrated sulfuric acid or by caustic fusion; separation of rare-earths by ion-exchange processes; conversion to halide salts; and reduction of the halide(s) to metal (See Dysprosium, Gadolinium and Erbium).

Bulk holmium metal is prepared by reduction of holmium chloride or fluoride by sodium, calcium, or magnesium in a tantalum crucible under argon atmosphere:



Pure holmium metal is obtained by distillation of crude metal at 1,500°C.

Reactions

Holmium forms all its compounds in +3 valence state. The metal forms fluoride, hydroxide, phosphate, oxalate, and carbonate that are insoluble in water. Its water-soluble salts are chloride, bromide, iodide, acetate, nitrate and sulfate.

Reactions with acids yield corresponding salts. Evaporation of the solutions yield water-soluble salts. Treatment with hydrochloric acid followed by evaporation of the solution yields a hexahydrate, $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$.

When heated with ammonium iodide, it forms holmium iodide, HoI_3 .

The bulk metal reacts with oxygen at high temperatures to yield Ho_2O_3 . The reaction is slow even at high temperatures. The finely divided metal, however, burns in oxygen at ordinary temperatures, glowing white-hot. It combines with hydrogen at elevated temperatures forming hydride, HoH_3 .

Analysis

Holmium may be measured in trace amounts by AA and ICP spectrophotometry, x-ray fluorescence, and neutron activation analysis.

HOLMIUM CHLORIDE

[10138-62-2]

Formula: HoCl_3 ; MW 271.29; also forms a hexahydrate, $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$, MW 379.38

Synonym: holmium trichloride

Uses

Holmium chloride is an intermediate for preparing holmium metal.

Physical Properties

Yellow monoclinic crystals; hygroscopic; density 3.7 g/cm³; melts at 718°C; vaporizes at 1,500°C; readily dissolves in water.

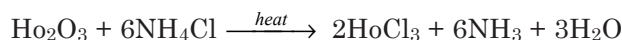
Thermochemical Properties

ΔH_f° (cry)	-240.3 kcal/mol
ΔH_f° (g)	-168.0 kcal/mol
ΔH_f° (hexahydrate)	-687.9 kcal/mol
ΔG_f° (hexahydrate)	-588.0 kcal/mol
S° (hexahydrate)	97.08 cal/degree mol
S° (g)	40.1 cal/degree mol
C_p (cry)	21.0 cal/degree mol
C_p (hexahydrate)	83.0 cal/degree mol
ΔH_{fus}	7.0 kcal/mol
ΔH_{vap}	44.0 kcal/mol

Preparation

Holmium chloride is obtained from rare-earth minerals. Recovery steps are discussed above (see Holmium). The rare-earth mineral is cracked by acid attack by heating with hydrochloric acid. The water-soluble chloride salt is filtered and separated from insoluble residues. The hydrated chloride salt is heated at 350°C in a current of hydrogen chloride to yield anhydrous HoCl₃. Heating in air in the absence of hydrogen chloride yields holmium oxychloride, HoOCl. Holmium chloride may be purified by distillation or vacuum sublimation.

Holmium chloride also can be prepared by heating holmium oxide with ammonium chloride:

**HOLMIUM OXIDE**

[12055-62-8]

Formula: Ho₂O₃; MW 377.86

Synonym: holmia; holmium sesquioxide

Occurrence and Uses

Holmium oxide occurs in nature, usually associated with small quantities of other rare-earth oxides. Commercial applications of this compound have not been explored fully. It is used in refractories and as a catalyst. Characteristic spectral emission lines of holmium oxide glass are used to calibrate spectrophotometers.

Physical Properties

Yellow cubic crystal; density 8.41 g.cm³; melts at 2,415°C; insoluble in

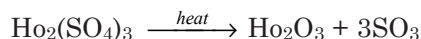
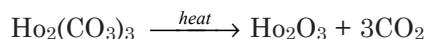
water; dissolves in acids (with reactions).

Thermochemical Properties

ΔH_f°	-449.5 kcal/mol
ΔG_f°	-428.1 kcal/mol
S°	37.8 cal/degree mol
C_p	27.5 cal/degree mol

Preparation

Holmium oxide is prepared by thermal decomposition of carbonate, oxalate, hydroxide, nitrate, sulfate, or any oxo salt of holmium:



The oxide may be obtained by direct combination of elements at elevated temperatures. The element in massive form, however, reacts slowly at high temperatures.

HYDRAZOIC ACID

[7782-79-8]

Formula: HN_3 ; MW 43.03

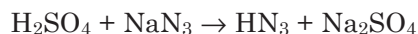
Synonyms: azoimide; hydroazoic acid; hydrogen azide.

Physical Properties

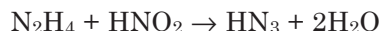
Colorless, volatile liquid; pungent disagreeable odor; density 1.09 g/mL; solidifies at -80°C ; boils at 37°C ; highly soluble in water; soluble in alkalies, alcohol and ether; pK_a 4.6 at 25°C .

Preparation

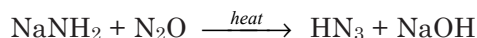
Hydrazoic acid is prepared by reacting sulfuric acid with sodium azide:



or by treating hydrazine with nitrous acid:

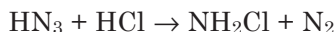


or by heating sodium amide with nitrous oxide:



Reactions

Hydrazoic acid reacts with mineral acids liberating nitrogen gas:



Reactions with oxidizing agents yield nitrogen and other products. Reactions with reducing agents yield various products including triazene, H_3N_3 , tetrazene, H_4N_4 , and ammonia, depending on reaction conditions.

HYDRAZINE

[302-01-2]

Formula: N_2H_4 ; MW 32.05

Structure: $\text{H}_2\text{N}-\text{NH}_2$, the N—N—H bond angle 112° and the N—N bond length 0.145 nm, sp^3 hybridization, tetrahedral, lone pair of electrons on the vertice of tetrahedron; dipole moment ~ 1.85 ;

Synonyms: hydrazine anhydrous; diamine

History and Uses

Hydrazine was isolated first as a sulfate salt by Curtius in 1887. Earlier, in 1875, Fischer prepared and identified the organic derivatives of hydrazine. Raschig in 1906 prepared hydrazine by hypochlorite oxidation of ammonia.

Hydrazine and its derivatives have numerous commercial applications. It was used initially as rocket propellant. During World War II, it was used as a fuel for rocket-powered fighter planes. However, the most important applications of hydrazine and its derivatives at present are: as blowing agents; for insect control; in pharmaceuticals; in water treatment; and in fuel cells. Hydrazine derivatives release nitrogen on decomposition, producing foaming action in polymers to form pores or cells. A large number of hydrazine derivatives are used in agricultural applications as fungicides, herbicides, and pesticides for weed and pest control. A few hydrazide drugs, such as isoniazid [54-85-3] are used extensively for treating tuberculosis. Other applications of hydrazine include its use in fuel cells; and in wastewater treatment for removal of iron; iron removal from hot-water heating systems; reduction of red iron oxide rust into magnetite; and for removal of oxygen to protect against corrosion. It also is used in electrolytic plating of metals on glasses and as a reducing agent. Several hydrazine derivatives are used in azo dyes; as coupling agents in color photography; and in explosives and ammunition primers.

Physical Properties

Colorless, mobile, fuming liquid; ammoniacal odor; density 1.0045 g/mL at 25°C ; refractive index 1.46044 at 22°C ; solidifies at 2°C to a white crystalline

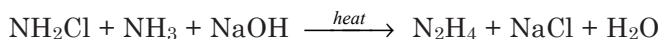
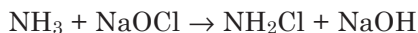
solid; boils at 113.5°C; flash point 52°C; burns with a violet flame; vapor pressure 14.4 torr at 25°C; critical temperature 379.85°C; critical pressure 145 atm; surface tension 66.67 dyne/cm at 25°C; dielectric constant 51.7 at 25°C; viscosity 0.876 centipoise at 25°C; very soluble in water; forms an azeotrope with water at molar composition of 58.5% hydrazine: 41.5% water (71.48%: 28.52% by weight), the azeotrope with water boils at 120.5°C; forms hydrazine hydrate at 1:1 molar concentration in water; soluble in alcohols and other polar solvents; pKa 8.1 at 25°C.

Thermochemical Properties

ΔH_f° (l)	-12.10 kcal/mol
ΔH_f° (g)	-22.80 kcal/mol
ΔG_f° (l)	-35.67 kcal/mol
ΔG_f° (g)	-38.07 kcal/mol
S° (l)	28.97 cal/degree mol
S° (g)	56.97 cal/degree mol
C_p (l)	23.63 cal/degree mol
C_p (g)	11.85 cal/degree mol
ΔH_{fus}	3.026 kcal/mol
ΔH_{vap}	10.82 kcal/mol
$\Delta H_{combust}$	-148.7 kcal/mol

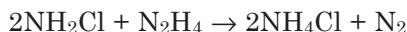
Production

Hydrazine may be produced by several methods. The most common commercial process is the Raschig process, involving partial oxidation of ammonia or urea with hypochlorite. Other oxidizing agents, such as chlorine or hydrogen peroxide may be used instead of hypochlorite. The reaction steps are as follows.



While the first partial reaction is rapid, the second reaction is slow at ordinary temperatures and, therefore, requires heating above 120°C.

The chloramines formed in the above reaction may further react with the product hydrazine, decomposing the latter to nitrogen.

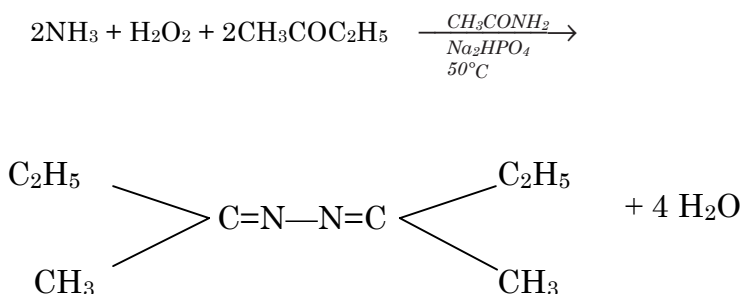


The above reaction is catalyzed by copper and other trace metal impurities and can be prevented by adding a suitable complexing agent. In a modification of the Raschig process, what is known as Olin-Raschig process, liquid chlorine feed is continuously absorbed in dilute NaOH solution forming sodium hypochlorite which, similar to the Raschig process, is made to react with

excess ammonia. The reaction is rapid. Further addition of large, excess anhydrous ammonia under pressure raises the temperature to about 130°C. This prevents any decomposition of hydrazine by chloramines.

In Ketazine processes, hydrazine derivatives are obtained first. Ammonia is oxidized by chlorine or chloramines in the presence of aliphatic ketones. The products are hydrazones and isohydrazones. These are converted to ketazines with excess ketone. The ketazines or the intermediate hydrazine derivatives may be hydrolyzed to hydrazine after all the oxidizing reactants, such as Cl_2 , NaOCl , or NH_2Cl are consumed. Unlike hydrazine, ketazines do not readily oxidize, and, therefore, the product yield is higher in these processes.

Several other processes have been developed. Most of these are based on oxidation of ammonia, using different oxidizing agents. In one such process, ammonia is oxidized with hydrogen peroxide in the presence of methyl ethyl ketone, acetamide and disodium hydrogen phosphate at 50°C:



Hydrazine also may be produced by oxidation of urea, NH_2CONH_2 , instead of ammonia.

Reactions

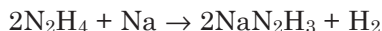
Hydrazine exhibits basic properties because of its lone pair of electrons on each nitrogen atom. Many of its reactions are analogous to those of ammonia.

Anhydrous hydrazine undergoes self-ionization to a small extent, yielding hydrazinium, hydrazide, N_2H_5^+ , and hydrazide, N_2H_3^- species:



The magnitude of K value for this self-ionization is in the order of 10^{-25} , which is greater than that for anhydrous ammonia ionizing to ammonium (NH_4^+) and amide (NH_2^-) ions ($K \sim 10^{-33}$). Anhydrous hydrazine thus forms salts with halide and other anions of the composition $\text{N}_2\text{H}_5^+ \text{X}^-$ which are acids. Similarly, metallic hydrazides, $\text{M}^+\text{N}_2\text{H}_3^-$, are bases in anhydrous hydrazine. Most hydrazine salts are unstable and are sensitive to heat and

shock. Reaction with sodium metal yields sodium hydrazide, NaN_2H_3 [13598-47-5] with liberation of hydrogen:



Reaction with sodium amide also yields the same compound with liberation of ammonia:



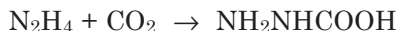
Hydrazide salts of alkaline earth metals, such as MgN_2H_2 and of aluminum, $\text{Al}(\text{N}_2\text{H}_3)_3$ are known and are less sensitive to heat and shock than are alkali metal hydrazides.

Reactions with alkali and alkaline earth metal hydrides also produce the same ionic metallic hydrazides:



Many metal alkyls undergo similar reactions forming their metal hydrazides.

Hydrazine reacts with carbon dioxide forming carbazic acid (hydrazinecarboxylic acid) [471-31-8]:

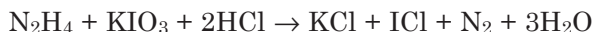


Oxidation-reduction reactions are probably the most important reactions of hydrazine. The compound can reduce several classes of inorganic substances including the oxidizing agents, metals and holoogens. Also, it can reduce a number of organic functional groups such as, carbonyl, nitro and nitrile groups.

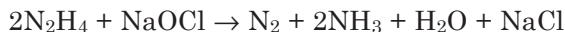
Chromate, dichromate, permanganate, chlorate and hypochlorite and other oxidants are readily reduced by hydrazine; for example, removal of chromate from wastewater may be achieved fully by converting water-soluble chromate to insoluble precipitate of chromium hydroxide, $\text{Cr}(\text{OH})_3$:



Hydrazine reduces potassium iodate in hydrochloric acid forming iodine monochloride, a reaction of analytical importance:

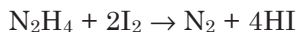
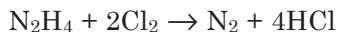


Hydrazine reduces sodium hypochlorite forming products that depend on molar ratios of the reactants. When hydrazine is in excess, ammonia is one of the products; but when hypochlorite is in excess, no ammonia is formed:

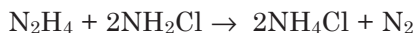




Hydrazine reacts with halogens forming hydrogen halides:



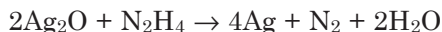
Hydrazine reacts with chloramines to produce ammonium chloride while decomposing to nitrogen. The reaction is catalyzed by metal ions at trace concentrations:



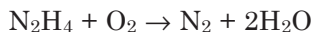
A reaction of commercial interest that is applied in many water treatment processes is for protection against corrosion. The reaction involves oxidation of iron to form magnetite that provides a protective coating on the metal surface:



Hydrazine reduces heavy metal oxides and their salts to free metals. These reactions are utilized for plating of metal films on plastics and glass:

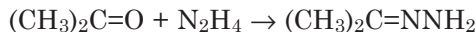


Hydrazine is a strong reducing agent. It reduces oxygen, forming nitrogen and water:

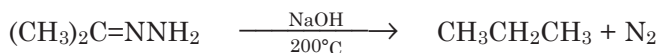


The reaction is highly exothermic ($H_{\text{rxn}} = -148.6$ kcal/mol) and is employed in rocket propellant engines and fuel cells.

An important reduction reaction is Wolff-Kishner reduction of carbonyl group on aldehydes and ketones to form hydrazones:

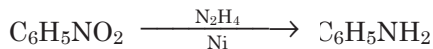


In the presence of a base and upon heating, the hydrazone yields alkane (or alcohols depending on reaction conditions):



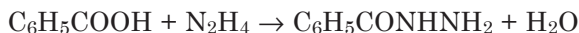
Diaziridines or isohydrazones may be obtained instead of hydrazones by varying the ratio of aldehyde or ketone to hydrazine.

Reduction of several classes of organics may be achieved using hydrazine and appropriate catalysts. It reduces nitro compounds to corresponding amines; e.g., nitrobenzene to aniline:

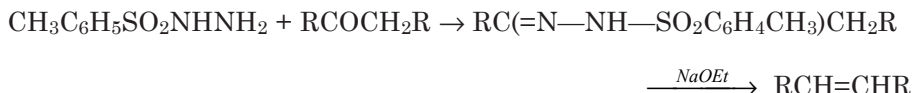


Nitro compounds in presence of carbonyl group are selectively reduced to amines in the presence of Raney nickel catalyst. Hydrazine reduces nitriles yielding hydrazones. Under controlled reaction conditions other functional groups, including nitroso and oxime, may be reduced. Many partially hydrogenated derivatives, such as azo-, hydrazo-, and azoxy compounds may be obtained by partial reduction with hydrazine. Reaction with chlorobenzene yields benzene.

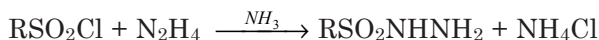
Reaction with benzoic acid yields benzoyl hydrazide:



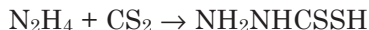
The product hydrazide may be sulfonated and decomposed by heating with a base in ethylene glycol to yield benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$. Many aromatic aldehydes may be produced by similar routes. The hydrazone derivative of toluenesulfonic acid reacts with an aldehyde or a ketone in the presence of a base catalyst, such as sodium ethoxide, to yield the corresponding olefin (Bamford-Stevens reaction):



Reactions with sulfonyl chloride in the presence of ammonia yield sulfonic acid hydrazides:



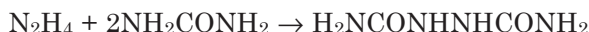
Hydrazine reacts with carbon disulfide to yield dithiocarbazic acid [471-32-9]:



In the presence of an alkyl halide and potassium hydroxide, dithiocarbazate ester is obtained. The product is used in many organic syntheses:



Refluxing an aqueous solution of urea and hydrazine yields hydrazodicarboxamide, $\text{H}_2\text{NC}(\text{=O})\text{NHNHC}(\text{=O})\text{NH}_2$ [110-21-4], which on chlorination yields azodicarbonamide $\text{H}_2\text{NC}(\text{=O})\text{N}=\text{NC}(\text{=O})\text{NH}_2$, used as a blowing agent for polymers:



Acetone cyanohydrin reacts with hydrazine forming a hydrazo derivative, $(\text{CH}_3)_2\text{C}(\text{CN})\text{NHNHC}(\text{CN})(\text{CH}_3)_2$ [6869-07-4], a precursor to azobis(isobutyronitrile), $(\text{CH}_3)_2\text{C}(\text{CN})\text{N}=\text{NC}(\text{CN})(\text{CH}_3)_2$, a blowing agent for PVC foam:



Thermal decomposition of hydrazine can occur by several energetic routes. The most favorable one being:



Under controlled conditions, hydrazine may be decomposed thermally to nitrogen and hydrogen:



Analysis

Hydrazine may be analyzed by various methods including GC-FID, GC-NPD, HPLC, GC/MS, polarography, colorimetry, and iodometric titrations. The iodometric method is simple and applicable to measure hydrazine quantitatively in water at all concentrations.

Hydrazine reduces iodine to hydrogen iodide. Thus, an excess of standard solution of iodine is added to a measured volume of aqueous hydrazine solution and the excess iodine is back titrated at pH 7.0 to 7.2 (buffered by sodium bicarbonate) against a standard solution of sodium thiosulfate using starch indicator.

Hydrazine solutions may be analyzed by various colorimetric methods. Low concentrations of hydrazine in aqueous samples at ppm level may be determined by treating the sample with an acidified solution of dimethylaminobenzaldehyde and the absorbance of color formed is measured at 485 nm with a spectrophotometer.

Hydrazine may be derivatized with salicylaldehyde to a hydrazone derivative, separated on a suitable HPLC column and determined by a UV detector. Aqueous samples may be directly injected into a polar GC column interfaced to an FID. Anhydrous hydrazine may be appropriately diluted in alcohol or ether and determined by GC/MS. The molecular ion for GC/MS determination by electron-impact ionization is 32.

Hazard

Hydrazine is a flammable liquid, and forms explosive mixtures with air in the range 4.7 to 99% hydrazine (by volume) in air. Violent reactions can occur when combined with oxidizing agents. Exposure to vapors or ingestion of the liquid can cause nausea, vomiting, and convulsion. Direct contact can cause eye damage. It also is a carcinogen and teratogen.

HYDRAZINE HYDRATE

[7803-57-8]

Formula: $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$; MW 50.06

Synonym: diamine hydrate

Uses

Hydrazine hydrate is used as a reducing agent in synthetic and analytical reactions and as a solvent for many inorganic compounds. It also is used with methanol as a propellant for rocket engines. Another application is catalytic decomposition of hydrogen peroxide.

Physical Properties

Colorless fuming liquid; faint odor; refractive index 1.4284; density 1.032 g/mL; boils at 119°C; solidifies at -51.7°C; miscible with water and alcohol; insoluble in chloroform, methylene chloride, and ether.

Preparation

Hydrazine hydrate is prepared by treating hydrazine sulfate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ with sodium hydroxide. The product is collected by distillation under nitrogen. It also is obtained as a by-product in the Bayer Ketazine process for producing hydrazine in which hydrazine solution is hydrolysed under pressure in a ketazine column.

Reactions

See Hydrazine.

Analysis

Elemental composition: H 12.09%, N 55.95%, O 31.96%. The compound may be identified from its physical properties. Its concentration can be determined by titration (See Hydrazine.)

Toxicity

Hydrazine hydrate is toxic by all routes of exposure. Toxic properties are similar to hydrazine (See Hydrazine.)

HYDRAZINE SULFATE

[10034-93-2]

Formula: $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$; MW 130.125

Uses

Hydrazine sulfate is used as a reducing agent; in analytical chemistry for gravimetric measurement of nickel, cobalt, and other metals, and in peptide analysis; in the separation of polonium from tellurium; as an antioxidant in

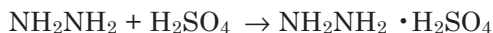
soldering flux for metals; in the preparation of hydrazine hydrate; and in many organic syntheses. It also is used as a fungicide.

Physical Properties

Colorless orthorhombic crystal; density 1.378 g/cm³; melts at 254°C; sparingly soluble in cold water 1.64% at 0°C and 3.41% at 25°C; more soluble in hot water; practically insoluble in alcohol (0.04% at 25°C).

Preparation

Hydrazine sulfate may be synthesized from aqueous ammonia and sodium hypochlorite solution in a two-step process. In the first stage, aqueous solution of ammonia is boiled with a normal solution of sodium hypochlorite in the presence of 10% gelatin solution to yield hydrazine. In the second stage, the hydrazine solution is ice-cooled followed by slow addition of concentrated sulfuric acid (Adams, R., and B.K. Brown. 1964. In *Organic Synthesis, Collective Volume I*, ed. H. Gilman and A. H. Blatt, 2nd ed. pp 309-310, New York: John Wiley & Sons). The reaction steps are as follows:



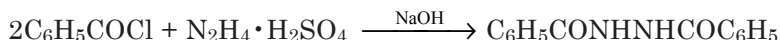
Reactions

Hydrazine sulfate, when distilled with caustic soda under nitrogen, yields hydrazine hydrate. The sulfate salt is used in many organic syntheses. A few synthetic reactions are listed below:

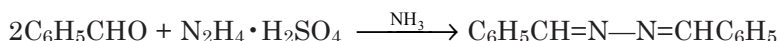
Reaction with 2,4-dinitrochlorobenzene and potassium acetate yields 2,4-dinitrophenylhydrazine:



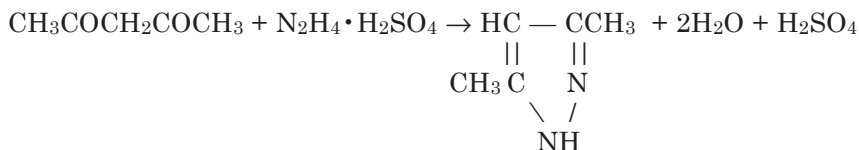
Hydrazine sulfate reacts with benzoyl chloride in basic medium to form dibenzoylhydrazine:



Reaction with benzaldehyde in ammonia forms benzalazine:



Hydrazine sulfate reacts with acetylacetone to yield 3,5-dimethylpyrazole:

**Toxicity**

Hydrazine sulfate is moderately toxic. Symptoms of ingestion are pares-
 thesis, somnolence, nausea, and vomiting. It also is an irritant to the eye. It
 is a confirmed carcinogen and an experimental teratogen.

HYDRAZINE HYDROCHLORIDE

[2644-70-4]

Formula: $\text{N}_2\text{H}_4 \cdot \text{HCl}$, MW 68.506

Synonym: hydrazine monochloride

Uses

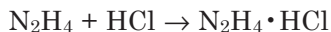
Hydrazine hydrochloride is used to prepare other hydrazine derivatives.

Physical Properties

White flakes; orthorhombic crystals; density 1.5 g/cm³; melts at 93°C;
 decomposes around 200°C; very soluble in water (37 g/100mL at 20°C); slight-
 ly soluble in alcohol.

Preparation

Hydrazine hydrochloride is prepared by the reaction of hydrazine with
 hydrogen chloride.

**Toxicity**

Hydrazine hydrochloride is moderately toxic by all routes of exposure. The
 oral LD₅₀ in mice is 126 mg/kg.

HYDROGEN

[1333-74-0]

Symbol: H; atomic number 1; atomic weight 1.0079; the lightest of all the
 chemical elements; the first element in the Periodic Table; Group IA (group 1)
 nonmetallic gaseous element; occurs as H₂, a diatomic molecule; electron con-
 figuration 1s¹; valences +1 and -1; three isotopes: H-1 or protium (99.9844%),
 H-2 or deuterium (0.0156%), H-3 or tritium (radioactive, t_{1/2} = 12.4 yr., in traces

only); molecular hydrogen is a mixture (ratio 3:1) of *ortho*- and *para*-hydrogen, which differ by the spins of their electrons and nuclei.

History, Occurrence, and Uses

The existence of hydrogen has been known since the 16th century. The gas, however, was reported in different ways, such as “inflammable air.” Henry Cavendish was the first to elucidate the chemical nature of hydrogen in 1776 and prepared it by several methods. Lavoisier in 1783 named this element hydrogen, which means, “water former.” Practically all gaseous hydrogen from earth’s atmosphere escaped into outer space during formation of the earth.

Hydrogen is the most abundant element in the universe. All stars primarily are made up of hydrogen, which undergoes nuclear fusion forming helium, and releasing an enormous quantity of energy. The sun constitutes about 80% hydrogen by mass. The concentration of hydrogen in the earth’s crust is estimated to be in the range of 1,400 mg/kg. Almost all hydrogen on earth is in the form of compounds. Its concentration in the atmosphere, however, is very small, about 0.00005%. The percentage composition of hydrogen in water, its most abundant compound on earth, is about 10.8% by mass. Although hydrogen is the fifteenth most abundant element on earth in mass, it forms the largest number of chemical compounds, more than any other element, including carbon. It is a component of all mineral acids, ammonia, natural gases and hydrocarbons, and a vast number of organic compounds from simple alcohols and aldehydes to complex proteins, carbohydrates, and chlorophyll.

Some important commercial applications of hydrogen gas include synthesis of ammonia by the Haber process; hydrogenation of vegetable oils, fats, and unsaturates; hydrocracking of petroleum crude; as a reducing agent in chemical reactions; in the manufacture of hydrochloric acid, methanol and metal hydrides; in oxy-hydrogen flame for welding and glass blowing; as a carrier gas in gas chromatography and a component of air-hydrogen flame in the Flame Ionization Detector (FID) in GC, and a filler gas in balloons and airships. It also is used in thermonuclear reactions and as a projectile proton in nuclear reactions. Liquid hydrogen is used as a cryogenic coolant, and in bubble chambers to study subatomic particles.

Physical Properties

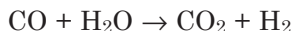
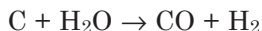
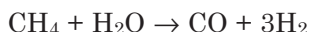
Colorless, odorless, tasteless gas; flammable; burns in air with a popping sound; the lower and upper explosive limits are 4 and 75%, respectively, by volume in air; autoignition temperature 574°C; lighter than air; density of the gas at 0°C and 1 atm 0.0899 g/L; density of liquid 70.8 g/L at –253°C, and the density of solid 76.0 g./cm³ at –262°C; liquefies at –252.9 °C and 1 atm; solidifies at –259.3°C and 1 atm; viscosity 0.0087 centipoise at 15°C and 1atm; critical temperature –240.18°C; critical pressure 12.76 atm; critical volume 65 cm³/mol; velocity of sound 1,269.5 m/sec at 0°C; diffusion coefficient in air at 0°C 0.634 cm²/sec; thermal neutron absorption cross section 0.332 barns; slightly soluble in water.

Thermochemical Properties

ΔH_f° (H ₂ gas)	0.0
ΔH_f° (H gas)	52.10 kcal/mol
ΔG_f° (H gas)	48.59 kcal/mol
S° (H ₂ gas)	31.24 cal/degree mol
S° (H gas)	27.41 cal/degree mol
C_p (H ₂ gas)	6.88 cal/degree mol
C_p (H gas)	4.97 cal/degree mol
ΔH_{fus} (H ₂)	0.0287 kcal/mol
ΔH_{vap} (H ₂)	0.210 kcal/mol
Thermal conductivity (at 0°C)	0.00038 cal/cm ² /sec/°C/cm

Production

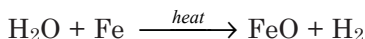
Hydrogen gas may be produced by several methods. It is commercially obtained by electrolysis of water. It also is made industrially by the reaction of steam with methane or coke:



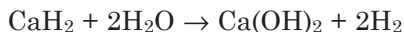
The reactions are carried out at about 900 to 1,000°C and catalyzed by nickel, nickel-alumina, or rhodium-alumina catalysts. In the laboratory, hydrogen may be prepared by the reaction of zinc or iron with dilute hydrochloric or sulfuric acid:



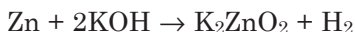
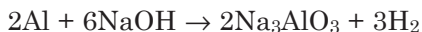
It also may be prepared by passing water vapor over heated iron:



Also, it can be generated by reaction of metal hydrides with water:



Another method of preparation involves heating aluminum, zinc, or other active metals in dilute sodium hydroxide or potassium hydroxide:

**Reactions**

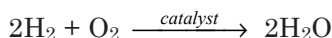
At ordinary temperatures, hydrogen gas is very stable. It's dissociation is

highly endothermic:

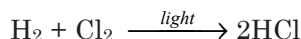


However, at higher temperatures or in the presence of a catalyst, it can combine with a number of metals and nonmetals forming corresponding binary compounds; such as H_2O , HF , HCl , HBr , HI , H_2S , NH_3 , CH_4 , PH_3 , AsH_3 , SbH_3 , SiH_4 , B_2H_6 , H_2Te , GeH_4 , and numerous metal hydrides. Some specific reactions are as follows:

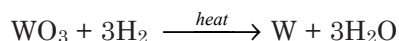
Hydrogen burns in air to form water. The reaction is catalyzed by Fe_2O_3 catalyst:



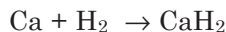
Reactions with halogens yield hydrogen halides.



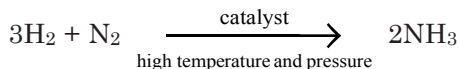
The reaction is explosive with fluorine and occurs under all conditions. With chlorine and bromine reaction occurs rapidly when exposed to light, undergoing a photochemical chain reaction. With iodine, the reaction is very slow, even at elevated temperatures. Hydrogen is a strong reducing agent. At high temperatures, the gas reduces many metal oxides to lower oxides or metals:



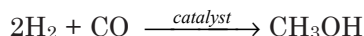
Hydrogen reacts with alkali and alkaline earth metals in the molten state to form their hydrides:



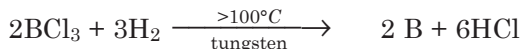
Hydrogen combines with nitrogen forming ammonia (See the Haber process.)



Reaction with carbon monoxide using copper/zinc oxide catalyst yields methanol:

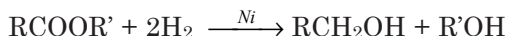


The above reaction is utilized in large-scale industrial production of methanol. Reaction with boron trichloride over a hot tungsten or tantalum filament yields boron and hydrogen chloride:



Hydrogen undergoes catalytic hydrogenation adding to unsaturated hydrocarbons, such as alkenes and alkynes forming alkanes. The reaction is catalyzed by nickel, platinum or palladium catalysts at ambient temperature. Hydrogenation of benzene over platinum catalyst yields cyclohexane, C_6H_{12} .

Hydrogen reduces esters into alcohols in the presence of nickel catalysts:



Many transition metal complexes catalyze homogeneous activation of molecular hydrogen in solution, forming hydrido complexes. Such complexes include pentacyanocobaltate(II) anion, $[\text{Co}(\text{CN})_5]^{3-}$, many metal carbonyls, and several complexes of rhodium, iridium, and palladium.

Analysis

Hydrogen gas may be analyzed by GC using a thermal conductivity detector (TCD). A molecular sieve 5Å capillary column and helium as the carrier gas should be suitable for analysis. A common method of analyzing hydrogen involves combustion with oxygen to produce water, which is trapped on an adsorbent and determined by gravimetry.

Hazard

Hydrogen is a flammable gas. It combines explosively with oxygen at ordinary temperatures in the presence of finely divided metals. The LEL and UEL are 4 to 74% by volume in air, respectively. It combines with halogens explosively. Explosion of its mixture with chlorine is detonated by sunlight, heat, or a spark.

HYDROGEN BROMIDE

[10035-10-6]

Formula: HBr ; MW 80.912. $\text{H}-\text{Br}$ bond energy 88.0 kcal/mol; internuclear distance 1.41Å; An aqueous solution of hydrogen bromide gas is hydrobromic acid.

Uses

Hydrobromic acid is used in the preparation of inorganic bromide salts. The acid also is used for many organic syntheses, including alkyl bromides from alcohols or olefins, and bromophenols from phenols. The compound also is used as an acid catalyst in many alkylation, selective oxidation, isomerization, and dehydrogenation reactions. Other applications are in extraction of minerals and use as a reducing agent.

Physical Properties

Colorless gas; fumes in moist air; pungent acrid odor; nonflammable; heavier than air; density 2.71 (air=1.0); gas density 3.55 g/L at 25°C; liquefies at -66.4°C; solidifies at -86.8°C; critical temperature 89.8°C; critical pressure 84.5 atm; highly soluble in water (saturated aqueous solution contains 66% HBr at 25°C); forms a constant-boiling azeotrope at 47.5% HBr in solution, boiling at 126°C at atmospheric pressure; soluble in alcohol; a 0.10*M* aqueous solution is 93% ionized to H⁺ and Br⁻ ions at 18°C.

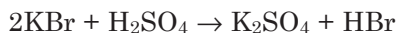
Thermochemical Properties

ΔH_f°	-8.676 kcal/mol
ΔG_f°	-12.763 kcal/mol
S°	47.49 cal/degree mol
C_p	6.96 cal/degree mol
ΔH_{fus}	0.576 kcal/mol
ΔH_{vap}	3.03 kcal/mol

Preparation

Hydrogen bromide gas may be produced by combustion of hydrogen in bromine vapor at 37.5°C using a catalyst such as platinized asbestos or platinized silica gel. Unreacted free bromine is removed from the product by passing the gaseous product mixture over hot activated charcoal. Hydrogen bromide formed may be absorbed in water to obtain the acid; or may be cooled and liquefied for shipment in cylinders.

Hydrobromic acid may be prepared in the laboratory by distillation of a solution of potassium bromide with dilute sulfuric acid:



The acid may be prepared by several other methods, as well, including reaction of bromine either with sulfur and water; or with phosphorus and water:



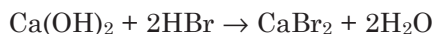
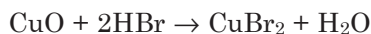
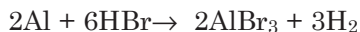
Hydrobromic acid also may be prepared by hydrogen exchange with a sodium or potassium bromide solution when the solution is passed through a cation-exchange resin.

Hydrobromic acid is stored and shipped in drums, tanks, carboys, or bottles, labeled as corrosive materials. The anhydrous gas is stored and shipped in cylinders under its vapor pressure.

Reactions

Hydrobromic acid is a strong acid which neutralizes bases forming salts and water. The most important reactions involve the formation of bromide salts. The acid reacts with most metals, their oxides, hydroxides, carbonates

and other salts, forming bromides:



Hydrogen bromide adds to carbon-carbon double bonds, usually the Markovnikov-type addition, forming bromo derivatives:



Analysis

Elemental composition: H 1.25%, Br 98.75%. The normality of the acid may be measured by titration against a standard solution of a base using a suitable color indicator or by potentiometric titration. The bromide ion, Br^- , may be measured quantitatively by ion chromatography after appropriate dilution. Concentration of HBr gas in air may be measured by passing a known volume of air through water and determining concentration of acid in aqueous solution by titration or ion chromatography. Alternatively, HBr gas may be analyzed by GC or GC/MS. A very polar column should be used for such measurements. An FID or a TCD type detector may be used for GC analysis.

Toxicity

Hydrogen bromide gas is a strong irritant to eyes, nose and respiratory tract. The acid is corrosive to skin.

HYDROGEN CHLORIDE

[7647-01-0]

Formula: HCl ; MW 36.461; a polar molecule, dipole moment 1.12D; $\text{H}-\text{Cl}$ bond energy 105.5 kcal/mol; internuclear distance 1.28Å. Hydrochloric acid is an aqueous solution of hydrogen chloride.

Synonym: muriatic acid

History and Uses

Basilus Valentinus of Italy was first to isolate the acid and reported it under the name spiritus salis in the fifteenth century. Glauber prepared this acid by the reaction of sulfuric acid with common salt in 1648. Lavoisier proposed the name muriatic acid in 1789 after muriate, the term referring to a chlorine-containing inorganic substance. Sir Humphrey Davy proved the gas was composed of only hydrogen and chlorine in 1810. Subsequently, the gas was named hydrogen chloride.

Dilute hydrochloric acid occurs in the stomachs of mammals. Gaseous hydrogen chloride occurs in trace concentrations in the atmosphere.

Hydrochloric acid is one of the most important industrial chemicals and has numerous applications. Both anhydrous hydrogen chloride and aqueous acid are used to produce a large number of chloride salts. The acid also is a common laboratory reagent. Some major applications of hydrochloric acid include processing of ores and extraction of metals from their minerals; in metal cleaning, particularly in steel pickling to dissolve oxide impurities; production of alumina, titanium dioxide, and other metal oxides by various hydrometallurgical processes; production of hydrogen; synthesis of chlorine dioxide; removal of heavy metal impurities from carbon black; activation of bentonite clays; etching of concrete surfaces for finishing operations; and as a catalyst in several organic reactions such as inversion of sugar, hydrolysis of starch to obtain sugar syrup, and esterification of aromatic acids.

Anhydrous hydrogen chloride gas is used to produce phosphonium chloride, PH_4Cl , which is a flame retardant for cotton textiles. Other major applications include manufacture of a number of high purity metal chlorides, ammonium chloride, chlorosulfuric acid; recovery of waste metals; preparation of alkyl chlorides and chloroacetic acids; and as a chlorinating agent in organic syntheses.

Physical Properties

Colorless gas; sharp pungent odor; fumes in air; nonflammable; refractive index of gas at 0°C 1.000446; density of the gas 1.639 g/L (1.268 times heavier than air); density of liquid at -155°C 1.045 g/cm³; density of solid at -192°C 1.507 g/cm³; liquefies at -85.05°C to a colorless liquid; freezes to a white crystalline solid at -114.22°C ; critical temperature 51.55°C ; critical pressure 82.01 atm; critical volume 81 cm³/mol; triple point -114.25°C ; dielectric constant at 25°C 1.0046; electrical conductivity 35.0 micromho/cm at -87.6°C ; highly soluble in water 42.02 g/100 g solution (or 72.47 g/100 g water) at 20°C and 1 atm; soluble in alcohols and ethers (47.0 g and 24.9 g/100 g solution at 20°C in methanol and ether, respectively.)

Hydrochloric acid is a colorless to yellowish liquid (the yellow coloration may be due to traces of iron, chlorine or organics contaminants); fumes in air; refractive index of 1.0 N solution 1.3417; density of commercial concentrated acid (37.8 g/100g solution) 1.19 g/mL, and constant boiling solution (20.22 g/100g solution) 1.096 g/mL at 25°C ; forms a constant boiling azeotrope with water at HCl concentration 20.22%; the azeotrope boils at 108.6°C ; several metal chlorides can be salted out of their aqueous solutions by addition of HCl; the addition of CaCl_2 can break the azeotrope; the pH of the acid at 1.0, 0.1 and 0.01 N concentrations are 0.10, 1.1, and 2.02, respectively; a 10.0 M solution ionizes to 92.6% at 18°C .

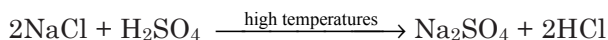
Thermochemical Properties

ΔH_f°	-22.06 kcal/mol
ΔG_f°	-22.78 kcal/mol
S°	44.67 cal/degree mol

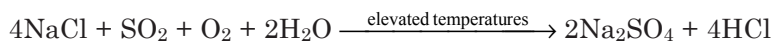
C_p	6.955 cal/degree mol
ΔH_{fus}	0.478 kcal/mol
ΔH_{vap}	3.86 kcal/mol
ΔH_{dissoc}	103.16 kcal/mol

Production

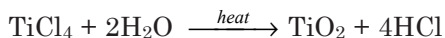
Hydrochloric acid can be produced by several methods. It is obtained from the reaction of sodium chloride and sulfuric acid in a cast iron retort at elevated temperature. Although reaction starts at 150°C, the complete reaction occurs at about 600°C:



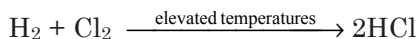
Hydrochloric acid also is made by the Hargreaves process in which a mixture of salt, sulfur dioxide, oxygen, and water are heated at elevated temperatures, between 430 to 540°C. The reaction is exothermic and becomes self-sustaining:



Hydrochloric acid may be produced by hydrolysis of metal chlorides such as titanium(IV) chloride:



High purity HCl for commerce is made directly from hydrogen and chlorine:



The above reaction is highly exothermic. The stoichiometric proportion of gaseous mixture at equilibrium flame temperature is cooled to 200°C, whereupon the elements combine rapidly to form HCl with over 99% yield.

HCl also may be prepared by several other methods including thermal dissociation of aluminum chloride hexahydrate, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, and as a by-product of manufacturing many organic compounds.

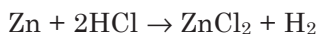
Crude HCl gas mixture may be purified by cooling and drying over concentrated sulfuric acid, which also removes organic unsaturated contaminants. Organic contaminants may be removed further by adsorption over molecular sieves, polystyrene foam, active carbon, or scrubbing with a high-boiling point organic liquid.

Commercial grade, concentrated hydrochloric acid is about 37.5% HCl by weight and has a normality of 12 and specific gravity 1.19.

Hydrogen chloride gas may be stored in steel cylinders free of contaminants. Monel, pure nickel, or its alloy, inconel, may also be used for storage and transportation up to 500°C. Hydrochloric acid may be stored in glass bottles or in containers made up of tantalum or tantalum-molybdenum alloys, or other alloys of zirconium, molybdenum, and tungsten.

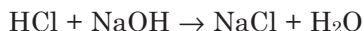
Reactions

Aqueous hydrochloric acid reacts with most metals and alloys liberating hydrogen and forming their chloride salts:

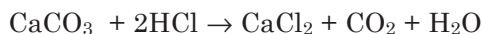


Reactions with highly electropositive elements (e.g. alkali metals) occur with explosive violence. On the other hand, certain metals, such as tantalum or tungsten, show little reactivity at ordinary temperatures.

Hydrochloric acid is a strong mineral acid, the pH of 0.1N HCl is 1.10. In aqueous solutions, it dissociates almost one hundred percent forming hydronium, H_3O^+ and Cl^- ion. The acid undergoes neutralization reactions with bases. With strong bases such as caustic soda solution, the neutralization is complete. The reaction may be written formally as:



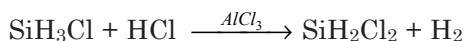
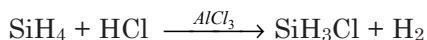
Reactions with metal carbonates liberate carbon dioxide:



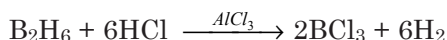
Anhydrous hydrogen chloride combines with ammonia or phosphine to form ammonium or phosphonium chloride:



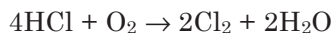
With silane or germane, the products are SiH_3Cl and SiH_2Cl_2 or GeH_3Cl and GeH_2Cl_2 , respectively:



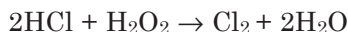
Reaction with diborane and other boron hydrides yield boron trichloride:



Hydrogen chloride gas reacts with oxygen forming chlorine and water:

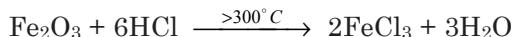
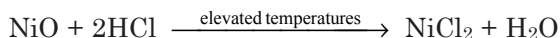


A similar reaction occurs with hydrogen peroxide:



At elevated temperature HCl gas reacts with metals forming chlorides. At ordinary temperatures the reaction is very slow.

Metal oxides react with hydrogen chloride at elevated temperatures forming corresponding metal chlorides and water:

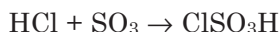


Often at high temperatures the reaction product is an oxychloride, particularly when the reactant is an oxide of a heavy transition metal, such as, hafnium or tungsten.

Reaction with nitric acid liberates chlorine gas:



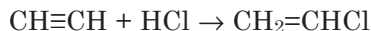
HCl forms adducts with anhydrous sulfates of several metals, such as $\text{ZnSO}_4 \cdot 2\text{HCl}$. HCl combines with sulfur trioxide to produce chlorosulfonic acid:



Hydrogen chloride undergoes addition reactions with carbon-carbon double and triple bonds. Many addition products of olefins and acetylenes are important industrial raw materials. It adds to ethylene forming ethyl chloride:



Addition of HCl to acetylene yields vinyl chloride:

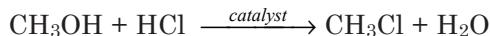


The product vinyl chloride can combine with another molecule of HCl to form 1,1-dichloroethane, undergoing Markovnikov addition:



HCl combines with many conjugated dienes forming a variety of addition products.

HCl reacts with methanol in the presence of a catalyst, such as FeCl_3 or ZnCl_2 , forming methyl chloride:



Usually all alcohols undergo such reactions, forming their alkyl halides and eliminating a molecule of water. The reaction is catalyzed by metal chlorides deposited on carbon, alumina or silica gel or by silica-alumina catalysts.

Analysis

The strength of hydrochloric acid solution can be measured by acid-base

titration against a standard solution of sodium hydroxide using a color indicator. Alternatively, the end point may be determined by potentiometric titration. Hydrogen chloride gas in air may be analysed by passing a measured volume of air through water containing methyl red or any suitable color indicator. Concentration of HCl in solution may be analysed using colorimetry by measuring absorbance of the solution. Hydrogen chloride in gaseous mixture may be analyzed by GC using a TCD or an FID and a strong polar column. HCl may be identified with a mass spectrometer following separation on a GC column. The characteristic mass ions for HCl should be 36 and 38.

Toxicity

Inhalation of HCl gas pungent-odor can cause coughing, choking, and irritation of the respiratory tract. Chronic exposure to the acid can produce gastritis and bronchitis. Ingestion of the acid can result in corrosion of the mouth and stomach, and diarrhea. Concentrated acid causes skin burn, and contact with eyes can damage vision.

HYDROGEN CYANIDE

[74-90-8]

Formula: HCN; MW 27.03

Structure: $\text{H}-\text{C}\equiv\text{N}$, a linear molecule with a carbon-nitrogen triple bond.

Synonyms: hydrocyanic acid; prussic acid; formonitrile

History and Uses

Hydrogen cyanide in pure form was prepared first in 1815 by Gay-Lussac. Earlier, in 1782, Scheel prepared this compound in dilute solution. The most important application of hydrogen cyanide is to produce methyl methacrylate for methacrylate resins and plastics. Other products made from hydrogen cyanide include potassium cyanide, sodium cyanide, adiponitrile, methionine, cyanuric chloride, cyanogen, nitrilotriacetic acid, and several triazine pesticides. The compound also is used in small amounts for extermination of rodents.

Physical Properties

Colorless liquid or gas; odor of bitter almond; burns in air with a blue flame; refractive index 1.2675; autoignition temperature 538°C; vapor density at 31°C 0.947 (air=1); liquid density 0.715 g/mL at 0°C and 0.688 g/mL at 20°C; boils at 25.7°C; melts at 13.24°C; vapor pressure 264 torr at 0°C; critical temperature 183.5°C; critical pressure 53.20 atm; critical volume 139 cm³/mol dielectric constant 158.1 at 0°C and 114.9 at 20°C; conductivity 3.3 mhos/cm at 25°C; viscosity 0.201 centipoise at 20°C; surface tension 19.68 dyn/cm; readily mixes with water and alcohols; density of a 10% aqueous solution 0.984 g/mL at 20°C; pK_a at 25°C 9.21.

Thermochemical Properties

ΔH_f° (liq)	26.03 kcal/mol
ΔH_f° (gas)	32.29 kcal/mol
ΔG_f° (liq)	29.88 kcal/mol
ΔG_f° (gas)	29.80 kcal/mol
S° (liq)	26.96 cal/degree mol
S° (gas)	48.23 cal/degree mol
C_p (liq)	16.87 cal/degree mol
C_p (gas)	8.58 cal/degree mol
ΔH_{fus}	2.01 kcal/mol
$\Delta H_{\text{combustion}}$	159.4 kcal/mol

Preparation

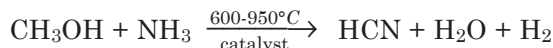
Hydrogen cyanide is generally produced in industrial quantities by high temperature catalytic reaction between ammonia, methane, and air (the Andrussow process). The stoichiometry of the process is:



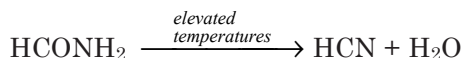
The above reaction is endothermic requiring a temperature of 1,100°C and a catalyst such as platinum or rhodium. Other hydrocarbons may be used instead of methane.

The compound may be made by several other methods, which include:

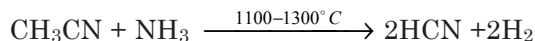
1. Heating methanol and ammonia in the absence of air at elevated temperatures (600 to 950°C) using a catalyst:



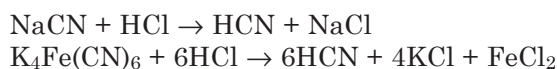
2. Thermal decomposition of formamide at elevated temperatures and reduced pressure:



3. Heating acetonitrile and ammonia at 1,100 to 1,300°C:



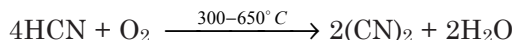
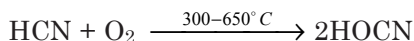
4. Reaction of sodium cyanide or potassium cyanide or potassium ferro cyanide with a mineral acid:



Reactions

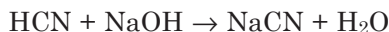
Hydrogen cyanide is a very weak acid, the pK_a at 25°C is 9.21

Hydrogen cyanide is oxidized by air when heated at elevated temperatures forming cyanic acid as the major product and cyanogen as a minor product. The reaction is catalyzed by gold and silver catalysts:

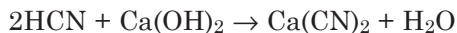


Oxidative cleavage over silver catalyst yields cyanogen.

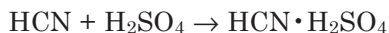
Reactions with caustic soda and caustic potash solution yield sodium cyanide and potassium cyanide, respectively:



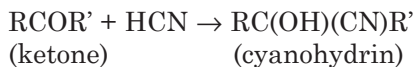
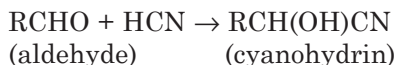
Similar reactions occur with some other metal hydroxides forming corresponding cyanides:



While treatment with aqueous sulfuric acid hydrolyzes hydrogen cyanide to formic acid, HCOOH , its reaction with concentrated sulfuric acid is violent forming an adduct $\text{HCN}:\text{H}_2\text{SO}_4$. The adduct is unstable, decomposing to carbon dioxide, sulfur dioxide and ammonia:



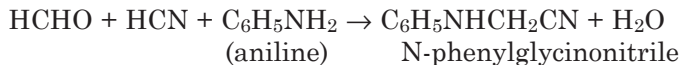
Hydrogen cyanide undergoes many important organic reactions forming a variety of industrial products. Probably the most important reaction is the addition of the carbonyl ($=\text{C}=\text{O}$) group. It adds to the carbonyl groups of aldehydes and most ketones forming cyanohydrins:



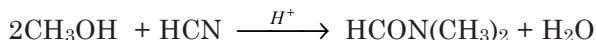
The above reaction is slow, but is catalyzed by mild bases. Thus, addition of potassium cyanide enhances the rate of reaction dramatically. Cyanohydrins are important intermediates in many organic synthesis.

Reaction with formaldehyde yields glycolic nitrile (a cyanohydrin), but in

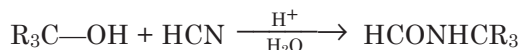
the presence of aniline the product is N-phenylglycinonitrile:



Reaction with methanol yields N,N-dimethylformamide:

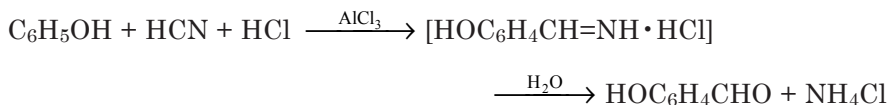


Reactions with secondary or tertiary alcohols in strongly acidic media yield amides (Ritter reaction):



Similarly, amines may be obtained by the addition of HCN to olefins.

Hydrogen cyanide reacts with phenol in the presence of hydrochloric acid and aluminum chloride, forming 4-hydroxybenzaldehyde:



Similar reactions occur with aromatic ethers, $\text{C}_6\text{H}_5\text{OR}$, giving aldehydes $\text{ROC}_6\text{H}_4\text{CHO}$ (Gattermann synthesis).

Analysis

Elemental composition: H 3.73%, C 44.44%, N 51.83%. HCN may be analyzed by GC or GC/MS. The aqueous solution may be directly injected onto the GC column and determined by an FID. For GC/MS determination, an alcoholic solution may be injected into the column. The characteristic mass ions are 27 and 26. The cyanide ion in aqueous solution also may be measured by cyanide ion-selective electrode, titrimetry, and by colorimetric methods (APHA, AWWA, WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association). For colorimetric analysis, the aqueous solution may be treated with a dilute caustic soda solution, followed by treatment with chloramine-T, and then with pyridine-barbituric acid reagent. A red-blue color develops, the absorbance of which is measured by spectrophotometer at 578 nm. The concentration of CN^- is determined from a standard calibration curve using KCN standards.

Titrimetric measurement involves titrating alkaline HCN solution against a standard solution of silver nitrate using a silver sensitive indicator, ρ -

dimethylaminobenzalrhodamine. At the end point, color changes from yellow to pink.

Hazard

Hydrogen cyanide is extremely toxic by ingestion, inhalation, skin absorption, and all routes of exposure. An oral dose of 50 mg could be lethal to humans (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed., New York: John Wiley). Symptoms from acute poisoning include labored breathing, shortness of breath, paralysis, unconsciousness, and respiratory failure. Lower doses can cause headache, nausea and vomiting. Oral LD₅₀ in mice is 3.7 mg/kg. Amyl nitrite is an effective antidote.

HCN also is a highly flammable compound; closed cup flash point is 0°C. The vapors form an explosive mixture with air: the LEL and UEL are 6 and 41% by volume of air, respectively.

HYDROGEN FLUORIDE

[7664-39-3]

Formula: HF; MW 20.006. A very stable polar covalent diatomic molecule; H—F bond energy 136.1 kcal/mol; at lower temperatures molecules are associated by hydrogen bonding; H—F bond length 0.92Å; partial ionic character 40%; dipole moment 6.10 D; hydrofluoric acid is an aqueous solution of hydrogen fluoride gas.

Synonyms: hydrofluoric acid gas; fluohydric acid gas.

History and Uses

Anhydrous hydrogen fluoride was first prepared by Fremy in 1856. It may have been made earlier in 1670 by Schwankhard in the process of etching glass using flourspar and acid.

Hydrogen fluoride is the most important fluorine compound, in terms of amounts produced and the vast number of uses. The largest application of this compound is in the manufacture of aluminum fluoride and sodium aluminum fluoride (cryolite) for electrolytic production of aluminum. Another major application is in the manufacture of chlorofluorocarbons, which are used as refrigerants and foaming agents; for making polymers; and for pressurizing gases. Another important application is in the processing of uranium where HF converts uranium dioxide to uranium tetrafluoride and hexafluoride, respectively. Uranium hexafluoride is used to separate isotopes of uranium by diffusion.

Hydrogen fluoride also is used as a catalyst in alkylation of aromatic compounds and for dimerization of isobutene. Other catalytic applications are in isomerization, polymerization, and dehydration reactions. Other uses are in

etching and polishing glasses for manufacturing light bulbs and TV tubes; in extraction of ores; in pickling stainless steel; in acidizing oil-wells; to remove laundry stains; for sample digestion in metal analysis; for removal of sand during metal castings; as a stabilizer for rocket propellant oxidizers; and in preparation of a number of fluoride salts of metals.

Physical Properties

Colorless gas or liquid at ambient temperatures; fumes in air; highly irritating; gas density 0.878 g/L at 25°C; liquid density 1.002 g/mL at 0°C; boils at 19.85°C; freezes at -83.55°C; vapor pressure 360 torr at 0°C; critical temperature 187.85°C; critical pressure 63.95 atm; critical volume 69 cm³/mol; viscosity 0.256 centipoise at 0°C; surface tension 10.1x10⁻⁴ dyn/cm at 0°C; dielectric constant 83.6 at 0°C; highly soluble in water and alcohols; forms an azeotrope with water at a composition 38.2 HF: 61.8 H₂O (weight percent); the azeotrope boils at 112.2°C; moderately soluble in benzene (2.55 g/100 g at 5°C).

Hydrofluoric acid is a colorless, fuming liquid which is an aqueous solution of hydrogen fluoride; densities of 20%, 40% and 60% acid at 20°C are 1.070, 1.135, and 1.215 g/mL, respectively; a 70% solution boils at 66.4°C; the same solution freezes at -69°C to a solid phase that has a composition of HF·H₂O; vapor pressure of 70% solution at 25°C 150 torr; partial pressures of HF over HF—H₂O solutions at 20°C are 0.412, 12.4 and 115.3 torr, respectively, for 20, 50 and 70% HF solutions by weight; equivalent conductance of 0.01 M and 0.1 M solutions at 20°C, 93.5 and 37.7 mhos-cm², respectively; a weak acid, pK_a 3.20 at 25°C; a 0.1M aqueous solution ionized <10%

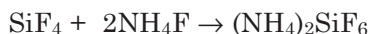
Thermochemical Properties

ΔH_f° (gas)	-65.32 kcal/mol
ΔH_f° (liquid)	-71.65 kcal/mol
ΔG_f° (gas)	-65.82 kcal/mol
S° (gas)	41.54 cal/degree mol
C_p (liquid at 16°C)	12.1 cal/degree mol
C_p (gas at 22°C)	109.0 cal/degree mol
ΔH_{vap}	1.80 kcal/mol
ΔH_{fus}	1.095 kcal/mol
ΔH_{soln}	-14.70 kcal/mol

Production

Hydrogen fluoride is produced from mineral fluor spar, CaF₂, which is decomposed by heating with concentrated sulfuric acid. The gaseous products consisting of hydrogen fluoride, sulfur dioxide, silicon tetrafluoride, and water vapor are separated from sulfuric acid mist and solid residues in a precondenser. The separation is carried out in a cyclone countercurrent scrubbing. Water is removed from the scrubbing fluid by the addition of 20% oleum. Hydrogen fluoride vapors are condensed and redistilled to obtain the product at 99.9% purity.

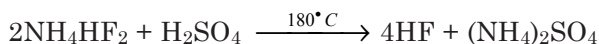
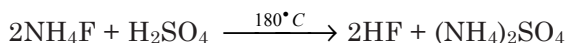
Hydrogen fluoride may be made from silicon tetrafluoride produced from phosphate rocks. A major step in the process involves reaction of silicon tetrafluoride with recycled ammonium fluoride solution:



The product ammonium fluorosilicate formed above is neutralized with ammonia solution to precipitate silica and form more ammonium fluoride:



The solution of ammonium fluoride is concentrated by evaporation to a solid residue which also contains a small amount of partially converted ammonium bifluoride, NH_4HF_2 . Heating this solid residue at 180°C with 95% sulfuric acid yields hydrogen fluoride:

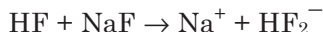


Hydrogen fluoride may be prepared by direct combination of hydrogen and fluorine at elevated temperatures. In general, HF can be generated by action of a concentrated acid with a fluoride salt.

Hydrofluoric acid must not be stored in glass or silicate ceramic containers. Stainless steel or PTFE are satisfactory for storage and handling. Nonferrous materials such as carbon, bronze, Monel or lead may be used for weaker acids.

Reactions

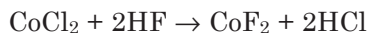
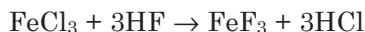
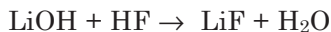
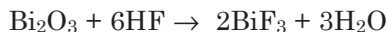
Although anhydrous hydrogen fluoride is a very strong acid, its aqueous solution, hydrofluoric acid, is weakly acidic, particularly when dilute. The K_a value of aqueous acid at 25°C is 6.46×10^{-4} mol/L. It is an excellent solvent for many inorganic fluorides, forming bifluoride anion:



At lower temperatures (below 200°C), HF forms molecular aggregates that are held by hydrogen bonding containing linear chains of $-\text{F}-\text{H}-\text{F}-\text{H}-\text{F}-\text{H}-$. However, above this temperature the weak hydrogen bond breaks producing monomolecular HF. Thermal dissociation of HF into elements probably occurs only at very high temperatures. Forty to 50% HF probably dissociates around $4,000^\circ\text{C}$, indicating that it is one of the most stable diatomic molecules.

The most important reactions of HF involve formation of inorganic fluoride

salts. HF gas or hydrofluoric acid reacts with oxides, hydroxides, carbonates, chlorides and other metal salts forming the corresponding fluorides. Some examples are:



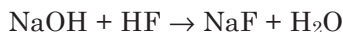
Reaction with potassium dichromate yields chromyl fluoride:



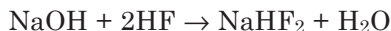
When ammonia gas is bubbled through a 40% ice-cold solution of hydrofluoric acid, the product is ammonium fluoride:



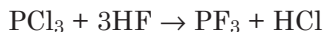
The addition of equimolar amount of NaOH or Na_2CO_3 to 40% HF instantaneously precipitates NaF:



Excess HF, however, yields sodium bifluoride, NaHF_2 :



Reaction with phosphorus trichloride yields phosphorus trifluoride; and with phosphoryl fluoride and sulfur trioxide, the product is phosphorus pentafluoride:



Analysis

Elemental composition: H 5.04%, F 94.96%. The total acidity of an aqueous HF solution may be measured by titration with a standard solution of base using phenolphthalein or another suitable color indicator. Alternatively, the end point may be determined by potentiometric titration. The fluoride ion may be analyzed using a fluoride ion-selective electrode or by ion chromatography. The HF gas may be analyzed by GC/MS using a GC column having

very high polarity.

Toxicity

Both anhydrous hydrogen fluoride gas and hydrofluoric acid are highly corrosive and dangerous. Skin contact by even dilute aqueous HF can be severely injurious, causing deep ulceration with delayed effect. The acid can penetrate the skin and destroy tissues. It also is damaging to eyes, nose and lungs. Inhalation can cause fluorosis and pulmonary edema.

HYDROGEN IODIDE

[10034-85-2]

Formula: HI; MW 127.91; H—I bond energy 71.0 kcal/mol; internuclear distance 1.62Å.

Hydriodic acid is the aqueous solution of hydrogen iodide.

Uses

Hydrogen iodide is used to prepare a number of organic iodides. Hydriodic acid is a reducing agent; and is used in the preparation of inorganic iodide salts. It also is used in pharmaceuticals; disinfectants, and as a reagent in chemical analysis.

Physical Properties

Colorless gas; pungent acrid odor; fumes in moist air; nonflammable; density 5.613 g/L; liquefies at -35.55°C ; density of liquid at -4.7°C 2.85 g/mL; solidifies at -50.8°C ; critical temperature 150.85°C ; critical pressure 82.01 atm; highly soluble in water, 234 g/100 g water at 10°C forming hydriodic acid; forms an azeotrope at 56.9% HI and 43.1% water; the azeotrope boils at 127°C and has density 1.709 g/mL; soluble in organic solvents.

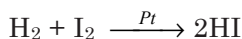
Hydriodic acid is a colorless liquid when pure or freshly prepared; becomes yellowish or brown on exposure to light or air; strong acid odor; pH of 0.1 molar solution, 1.0; a 0.1 M aqueous solution is 95% ionized at 25°C ; miscible with alcohols; dissolves iodine.

Thermochemical Properties

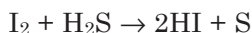
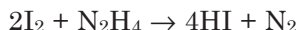
ΔH_f°	6.33 kcal/mol
ΔG_f°	0.406 kcal/mol
S°	49.38 cal/degree mol
C_p	6.98 cal/degree mol
ΔH_{vap}	4.723 kcal/mol
ΔH_{fus}	0.686 kcal/mol

Preparation

Hydrogen iodide is prepared by direct combination of hydrogen and iodine vapor in the presence of platinum catalyst:



The compound is produced in commercial scale by reaction of iodine with hydrazine or hydrogen sulfide:



Hydriodic acid may be prepared by dissolving hydrogen iodide gas in water. The acid also may be obtained by electrolysis of iodine solution or by passing hydrogen sulfide into a suspension of iodine in water and boiling to expel excess sulfide. After boiling, the precipitated sulfur is removed by filtration through fritted glass plate or glass wool.

Hydriodic acid in small quantities may be prepared by adding water carefully to a solid mixture of red phosphorus and iodine.

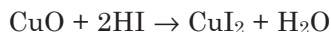
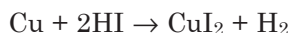
Technical grade hydriodic acid is a 47% HI solution and usually has a brown color due to the presence of free iodine, produced by air oxidation of HI. Hydriodic acid should be stored in the dark to prevent photochemical decomposition, and free from air to prevent oxidation. The addition of 1.5% hypophosphorus acid (H_3PO_2) prevents oxidative decomposition.

Hydriodic acid also is commercially sold at 57% (azeotropic concentration) and 10% aqueous solutions.

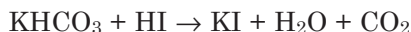
Reactions

Hydrogen iodide gas dissociates on heating to hydrogen and iodine.

Hydrogen iodide in gaseous state or in the aqueous solution (hydriodic acid) reacts with most metals and their salts. Hydriodic acid dissolves metals and metal oxides, forming iodide salts:



HI also reacts with metal salts, forming iodides:



Hydriodic acid is a strong reducing agent, which readily reduces oxidizing substances. Reaction with oxygen yields iodine:



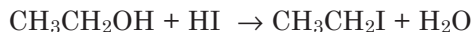
Hydrogen iodide adds to double bond of alkenes undergoing Markovnikov addition. The reaction is faster than that with other hydrogen halides:



HI replaces iodine from organic iodo compounds:



Reactions with lower alcohols yield alkyl iodides:



Analysis

Elemental composition: I 99.21%, H 0.79%

The strength of hydriodic acid may be measured by titrating against a standard solution of base using color indicator, or by potentiometric titration. It can be analyzed by treatment with an oxidizing agent such as chlorine and the liberated iodine is titrated with a standard solution of sodium thiosulfate using starch indicator. The blue color of the solution decolorizes at the end point. Hydrogen iodide gas may be measured by GC-TCD using a very polar column. Also, it may be identified by GC/MS, the molecular ion having mass 127.

Toxicity

The gas is a strong irritant to eyes, nose and mucous membranes. The acid is corrosive to skin.

HYDROGEN PEROXIDE

[7722-84-1]

Formula: H_2O_2 ; MW 34.015

Structure: $\text{H}-\text{O}-\text{O}-\text{H}$, covalently bound, nonpolar molecule.

Synonyms: hydrogen dioxide; perone; hydroperoxide.

History and Uses

Hydrogen peroxide was prepared first by Thenard in 1818. It has many industrial applications. Aqueous solutions at varying concentrations are used for bleaching fabrics, silks, furs, feathers and hair; as a dough conditioner; and a bleaching and oxidizing agent in foods; for cleaning metals; as a laboratory reagent for oxidation; as an antiseptic; in sewage and wastewater treatment; and in preparation of inorganic and organic peroxides. An 80% concentrated solution is used in rocket propulsion.

Physical Properties

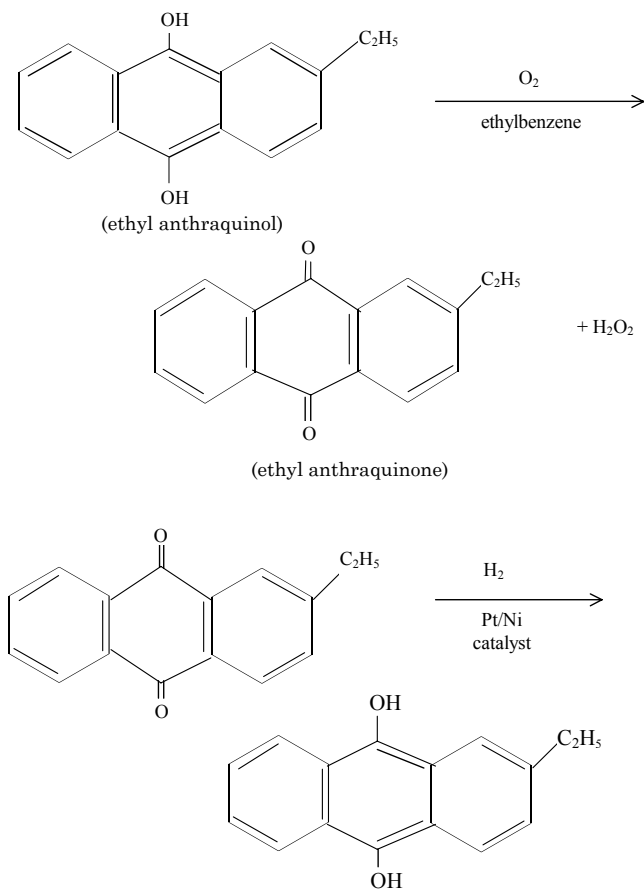
Colorless liquid; pure compound or 90% solution unstable; bitter taste; density 1.463 g/mL; boils at 150.2°C; freezes at -0.43°C; vapor pressure 9.9 torr at 50°C and 121.5 torr at 100°C; viscosity 1.245 centipoise at 20°C; surface tension 80.4 dyn/cm at 20°C; miscible with water in all proportions; soluble in ether; densities of 30%, 70%, and 90% H₂O₂ solutions are 1.1081, 1.2839 and 1.3867 g/mL, respectively, at 25°C; freezing points at these concentrations are -25.7°C, -40.3°C and -11.5°C, respectively; and their boiling points are 106.2°C, 125.5°C and 141.3°C, respectively; decomposed by many organic solvents; pK_a at 25°C is 11.62.

Thermochemical Properties

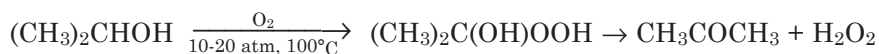
ΔH_f° (liq)	-44.885 kcal/mol
ΔH_f° (gas)	-32.576 kcal/mol
ΔG_f° (liq)	-28.776 kcal/mol
ΔG_f° (gas)	-25.239 kcal/mol
S° (liq)	55.62 cal/degree mol
S° (liq)	55.62 cal/degree mol
S° (gas)	37.05 cal/degree mol
C _p (liq)	10.3 cal/degree mol
ΔH_{vap} (at 25°C)	12.33 kcal/mol
ΔH_{fus}	2.988 kcal/mol
ΔH_{dissoc}	8.20 kcal/mol

Preparation

Hydrogen peroxide is commercially produced by autooxidation of ethyl anthraquinol in a solvent such as toluene or ethylbenzene. The product ethyl anthraquinone is reduced by hydrogen over supported nickel or platinum catalyst to regenerate back the starting material, ethyl anthraquinol for a continuous production of H₂O₂. The reaction steps are:

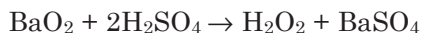


Hydrogen peroxide may also be made by heating 2-propanol with oxygen at 100°C under 10 to 20 atm pressure:

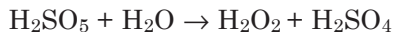
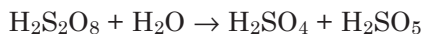
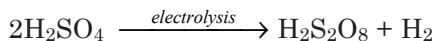


Vapor phase partial oxidation of hydrocarbons also yield H_2O_2 . However, several by-products are generated, the separations of which make the process difficult and uneconomical.

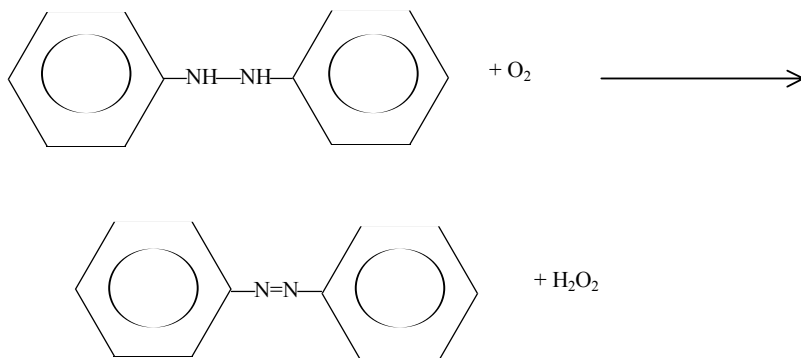
Hydrogen peroxide may also be prepared by treating barium peroxide with dilute sulfuric acid:



Another preparative method involves electrolytic conversion of aqueous sulfuric acid to peroxydisulfate followed by hydrolysis to H_2O_2 (Weissenstein process). The reaction steps are as follows:



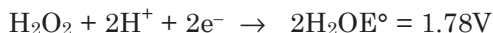
An earlier method, which currently is no longer practiced commercially, involved oxidation of phenyl hydrazine:



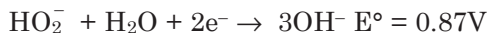
Hydrogen peroxide obtained this way may contain many impurities, depending on the process used. Such impurities are removed by ion exchange, solvent extraction, and distillation. Dilute solutions of H₂O₂ may be purified and concentrated by fractional distillation at reduced pressures.

Reactions

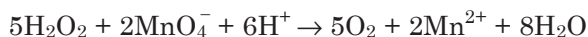
The most important reactions of hydrogen peroxide involve oxidation-reduction. It is a powerful oxidizing agent, both in acidic and basic solutions. Usually a 30% aqueous solution of H₂O₂ is used in oxidation. While oxidation with H₂O₂ in basic solution is fast, it is slow in acid solution. The half-reaction in acidic solution is:



The half-reaction for the basic HO₂⁻ ion is



However, H₂O₂ will behave as a reducing agent only towards a very strong oxidizing agent, such as MnO₄⁻:

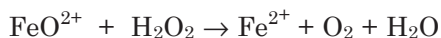
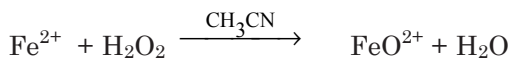


H_2O_2 is more acidic than water in dilute aqueous solution. The equilibrium constant K at 20°C is about 1.5×10^{-12} for dissociation of H_2O_2 to H^+ and HO_2^- . The pH of a 50% aqueous solution is 4.3.

Aqueous solution of H_2O_2 decomposes into water and oxygen upon boiling:

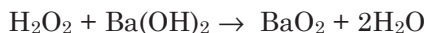
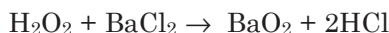


The reaction is exothermic, ΔH_{rxn} being -23.66 kcal. In basic solution, such decomposition occurs very rapidly. Also, decomposition is catalyzed rapidly by trace amounts of transition metals. In aqueous media, Fe^{2+} ion decomposes H_2O_2 forming $\text{Fe}^{\text{III}}(\text{OH})_2^+$ and OH^- ions, while in acetonitrile a “ferryl” ion, FeO_2^{2+} is formed initially, but it reverts to Fe^{2+} ion. The reactions are:

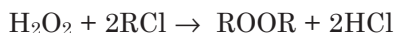
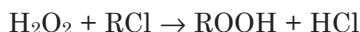


(Cotton, F. A., G. Wilkinson, C. A. Murillo, and F. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed., New York: John Wiley).

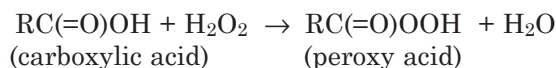
Reaction with sulfuric acid yields monoperoxysulfuric acid. Reactions with many alkaline earth compounds yield peroxides of alkaline earth metals:



Hydrogen peroxide undergoes substitution reactions with alkyl halides forming an organic peroxy acid or peroxide, depending on reaction conditions and molar ratios of reactants. The mechanism of such reactions are very complex. These reactions may be represented in the following equations:



Reactions with carboxylic acids yield peroxy acids:



Reaction with acetyl chloride yields diacetyl peroxide. Similar diacyl peroxides are formed from other acyl chlorides:



Reactions with ketones yield ketone peroxides. For example, with methyl ethyl ketone, the product is methyl ethyl ketone peroxide, which probably is a mixture of monomeric and polymeric products of peroxidic structure.

These organic peroxides are sensitive to shock and heat and require careful handling.

Hazard

Hydrogen peroxide is a strong oxidizing agent. Concentrated solutions, even a 30% aqueous solution, should be handled carefully. The compound decomposes violently in the presence of trace impurities. Inhibitors are, therefore, added at trace levels to prevent decomposition. Explosion can occur when concentrated solutions are heated or brought in contact with a number of organic substances that are readily oxidizable or that form organic peroxides, such as alcohols, aldehydes, ketones, anhydrides, and carboxylic acids (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons). Also, reactions with metals, metal alloys, a number of metal salts and oxides, and concentrated mineral acids can proceed to explosive violence.

HYDROGEN SELENIDE

[7783-07-5]

Formula: H_2Se ; MW 80.98

Uses

Hydrogen selenide is used in preparation of metal selenides and organoselenium derivatives. It also is used in doping mix for semiconductor applications.

Physical Properties

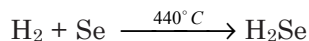
Colorless gas; disagreeable odor; flammable; gas density 3.553 g/L; liquefies at -41.25°C ; liquid density 2.12 g/mL at -42°C ; freezes at -65.73°C ; critical temperature 137.85°C ; critical pressure 88.0 atm; soluble in water, carbon disulfide and phosgene; pK_a 3.89 and 11.0 at 25°C , respectively, for the first and second replaceable hydrogen.

Thermochemical Properties

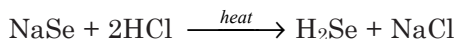
ΔH_f°	7.10 kcal/mol
ΔG_f°	3.80 kcal/mol
S°	52.34 cal/degree mol
C_p	8.29 cal/degree mol
ΔH_{vap}	4.71 kcal/mol

Preparation

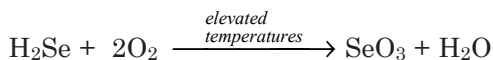
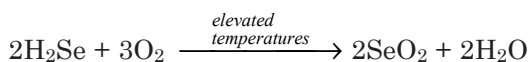
Hydrogen selenide may be synthesized directly from elements by heating at elevated temperatures. It is prepared by heating hydrogen at 440°C with either selenium metal in a sealed tube or with selenium vapor over pumice stone:



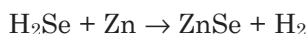
Alternatively, the compound may be prepared by treating an alkali metal selenide with hydrochloric acid during mild heating:

**Reactions**

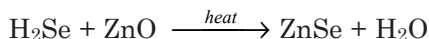
Heating with oxygen at elevated temperatures decomposes hydrogen selenide forming selenium oxides and water:



Hydrogen selenide reacts with most metals forming metal selenides with the liberation of hydrogen:



Metal oxides are converted to metal selenides on heating:

**Analysis**

Elemental composition: H 2.49%, Se 97.51%. The gas may be analyzed by GC using a TCD, FID or a flame photometric detector. The compound may be identified by GC/MS: the molecular ions have masses 82 and 80. The compound may be absorbed in water and the solution analyzed for elemental selenium by flame or furnace atomic absorption—or by ICP atomic emission spectrophotometry.

Hazard

Dangerously toxic by inhalation. Exposure can cause injury to lungs and liver; pneumonitis, and strong irritant actions on skin, eyes, and mucous membranes. Other effects are garlic odor of breath, nausea and dizziness. A few minutes exposure to 50-100 ppm concentration of this gas in the air can be lethal to humans. LC₅₀ inhalation (rat): 20 mg/m³/1 hr.

Hydrogen selenide is flammable, forming an explosive mixtures with air.